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Control Technology Alternatives and Costs for Compliance: Elemental Phosphorus Plants

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CONTROL TECHNOLOGY ALTERNATIVES AND COSTS FOR COMPLIANCE - ELEMENTAL PHOSPHORUS PLANTS

FINAL REPORT TO THE
ENVIRONMENTAL PROTECTION AGENCY

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ABSTRACT

On April 6, 1983, the United States Environmental Protection Agency (EPA) proposed a standard under Section 112 of the Clean Air Act limiting airborne polonium-210 emissions for calciner operations at domestic elemental phosphorus plants to 1 Ci/yr. To evalute the effect of the proposed standard, physical and chemical properties of polonium are reviewed and transport characteristics of polonium through plant processes assessed. Results indicate that polonium is volatilized from phosphate ore during calcining and, for the most part, deposited on fine particulates leaving the process. Projected emissions for each elemental phosphorus plant were determined using available data, and the uncertainty associated with each estimated release was evaluated. After taking into account this uncertainty, two plants were determined to exceed the proposed limiting standard for airborne polonium emissions. One plant was found in borderline compliance.

Emission control alternatives are proposed for the three plants. Cost estimates associated with each proposed alternative are provided.

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1.0 SUMMARY

This report projects airborne polonium-210 emissions from calcining operations at each of eight domestic elemental phosphorus plants, presents an uncertainty analysis for each projected polonium emission, and specifies the current status of compliance of each plant with respect to a proposed Environmental Protection Agency (EPA) standard limiting airborne polonium emissions to 1 Ci/yr. Two plants are projected as being out of compliance with emissions greater than 1 Ci/yr. One plant is considered in borderline compliance with an emission of slightly less than 1 Ci/yr.

To propose airborne polonium emission control strategies, each of the three plants was examined with respect to polonium transport through the elemental phosphorus production process. The results of these analyses indicate that polonium contained in phosphate ore may be volatized in calcining operations and subsequently condensed onto the particulates generated during these processes. Since fine particulates (less than 1 micron diameter) have a greater surface area to mass ratio than larger particulates, the polonium is enriched on the fine particulates. A literature search was conducted that produced information detailing this type of transport for polonium and other elements.

Since most of the volatilized polonium ultimately resides on fine particulates leaving the calcining operations, proposed equipment control strategies for each plant were determined by evaluating the collection efficiency in the 0.1 to 1.0 micron diameter region of available particulate control technologies. The two general types of technologies determined applicable are barrier filters and electrostatic precipitation. These techniques represent the only commercially available processes for fine particulate control applicable to large industrial gas streams. Proposed administrative control strategies for the plant determined in borderline compliance include control of polonium input to the calcining operations and control of annual elemental phosphorus production rate.

Cost estimates are presented for all equipment-related control alternatives proposed and include pertinent costs, such as capital, operating, maintenance, retrofit, and implementation. For the out-of-compliance plants, estimated capital costs range from $7 to $11 million for an appropriately sized baghouse filter system and from $10 to $16 million for an electrostatic precipitation unit. Cost estimates are also provided for the equipment-related and administrative control alternatives proposed for the borderline compliance plant.

The areas of engineering uncertainty with respect to compliance are the description of polonium transport within the plants and the process design of equipment for fine particulate control. Since adequate detail on polonium transport phenomena is unavailable, a specific design criterion for the process design of control equipment cannot be determined. In addition, since the polonium apparently resides preferentially on the fine particulates, recovery of polonium cannot be accurately predicted because of the uncertainty associated with the use of process design equations to predict fine particulate recovery. The only way to reasonably ensure equipment performance is to conduct actual pilot tests. This would involve routing of a slip stream from an operating plant through prototype control equipment and measuring the polonium recovery efficiency.

2.0 INTRODUCTION

The elemental phosphorus industry is neither regulated nor monitored for the possession, use, or discharge of radioactive materials associated with phosphate rock and its products and by-products. On April 6, 1983, the U. S. Environmental Protection Agency (EPA) proposed a standard limiting the airborne emissions of Po-210 in elemental phosphorus plant calciner offgases to 1 Ci/yr [1].

The objectives of this report are to review the status of compliance of existing elemental phosphorus plants with the proposed standard, examine the administrative procedures control technology necessary to bring problem plants into compliance, and estimate the costs associated with achieving such compliance.

To meet these objectives, the report first presents projected releases based on general background information. Next, the uncertainties associated with the releases are calculated. Taking into account these uncertainties, the compliance status for each of the eight U.S. elemental phosphorus plants is then determined. Each out-of-compliance and borderline compliance plant is further evaluated emphasizing polonium transport considerations. For each of these plants, potential administrative controls and emission control equipment additions or modifications are examined. The costs for each viable alternative are estimated.

3.0 BACKGROUND

3.1 RADIONUCLIDES IN PHOSPHATE ORES

Phosphate ore deposits are located in three principal regions of the United States:

- Southeastern region (mainly Florida, but also South Carolina, North Carolina, and Georgia)
- Northern Rocky Mountain region of eastern Idaho, western Wyoming, northern Utah, and southwestern Montana
- Middle Tennessee

Most of this country's marketable phosphate rock is produced in Florida, but most of the ore used in elemental phosphorus production is from the other regions. The phosphate ores from the three principal regions are distinct in their radiological characteristics. Generally, ores from the southeastern region have the highest radionuclide concentrations, followed respectively by those from the northern Rocky Mountain region and those from middle Tennessee. The radioactivity content of phosphate rocks from different deposits within the same general region, however, may vary widely. Most of the natural radioactivity present is represented by the uranium series radionuclides (Figure 3-1), although some phosphate rocks also contain elevated levels of thorium and its daughter products. Uranium-238 is a primordial radionuclide that heads a series of heavy radioactive atoms. If a phosphate deposit is sufficently old and has not been subjected to physical or chemical separation processes, the radionuclides present should be in a state of radioactive equilibrium, wherein the rate of decay of each radionuclide is very nearly equal to that of the parent U-238. Table 3-1 gives radionuclide concentration data for phosphate rocks of various geographic

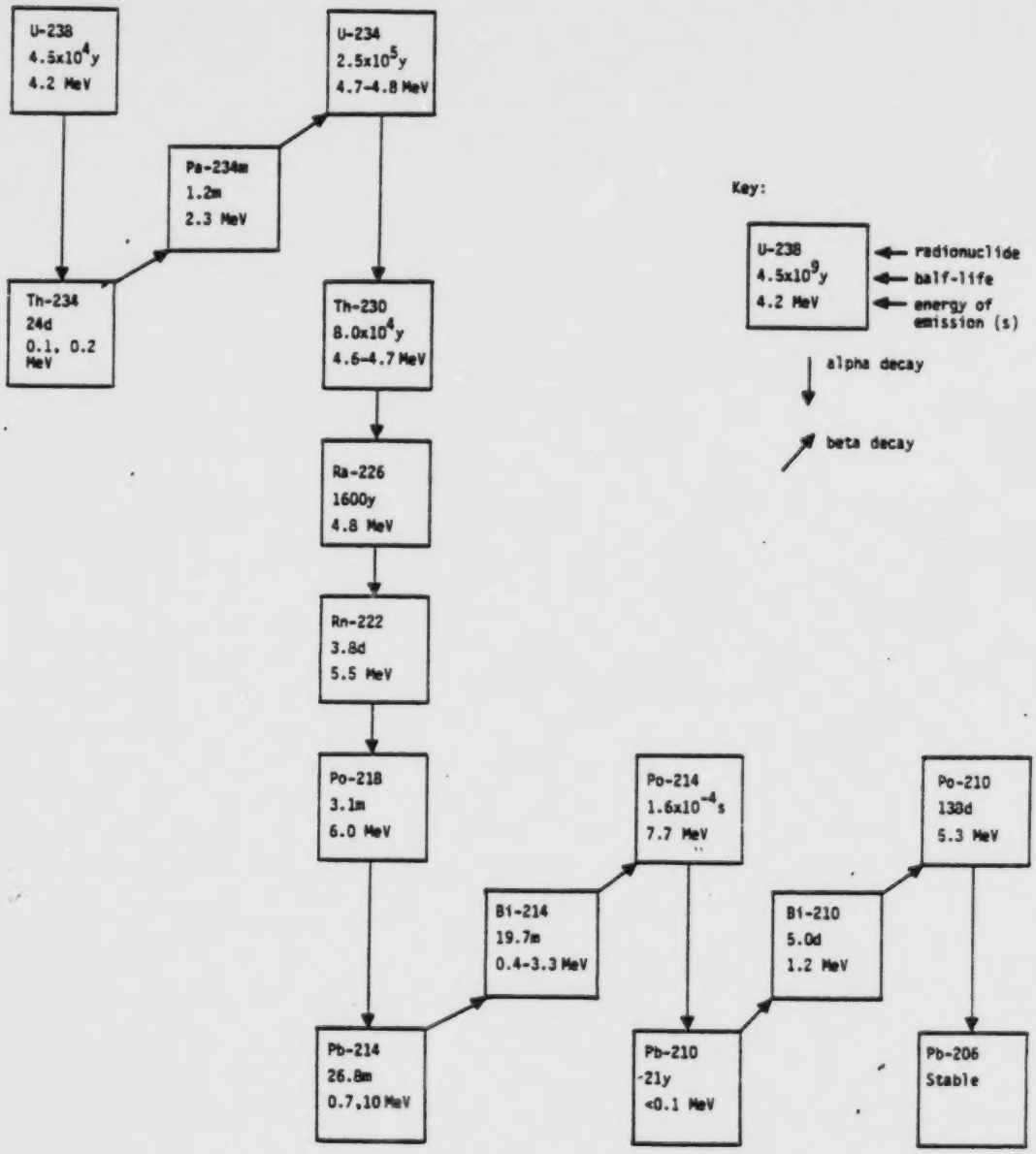


Figure 3-1. The Uranium Decay Series.

Table 3-1. Radionuclide Concentrations in Phosphate Rocks of Various Origins.

Origin	Type of Material	No. Samples	Radionuclide Concentration (pCi/g)			Remarks
			U-238	Ra-226	Th-232	
Florida	Pebble	11	69	73	1.5	Data are from Ref. [2]; concentration data are median values and are converted to pCi/g from reported units of ng/kg or mg/kg
		4	73	74	1.2	
		14	49	53	1.4	
	Soft phosphate	12	42	43	1.9	
	Miscellaneous phosphate	7	34	31	2.1	
		9	25	21	1.9	
North Florida	Mining land matrix	4	NS(1)	8.6	NS	Data are from Ref. [3]; concentration data are mean values and are reported on dry weight basis
	Pebble	1	NS	26	NS	
	Rock concentrate	4	NS	17	NS	
Central Florida	Mining land matrix	6	NS	38	NS	
	Pebble	13	NS	57	NS	
	Rock concentrate	12	NS	35	NS	
North Florida	Mining land matrix	NS	7.6	8.6	NS	Data are from Ref. [4]; concentration data are mean values of composite samples
Central Florida	Mining land matrix	NS	20	18	NS	
Florida	Marketable phosphate rock	NS	41	42	0.5	Data are from Ref. [5]
Tennessee	Brown rock	17	3.6	4	0.7	Data are from Ref. [2] and are median values converted to pCi/g from reported units of ng/kg or mg/kg
		8	4.3	4	0.6	
		3	3.3	4	0.7	
Tennessee	Blue rock	3	5.3	7	0.3	
	White rock	4	3.3	5	0.2	
	Phosphatic limestone	3	2.6	3	0.2	
South Carolina	Phosphate	11	132	133	2.1	
North Carolina	Phosphate	3	25	18	1.0	
Arkansas	Phosphate	13	9.9	11	1.4	
Oklahoma	Phosphate	5	8.3	10	0.9	
Montana	Phosphate	10	38	41	0.8	
Idaho	Phosphate	5	50	49	0.9	
Wyoming	Phosphate	4	60	62	1.3	
Utah	Phosphate	9	42	50	0.8	

(1) NS = Not specified

origins. The table indicates that the uranium series radionuclides in phosphate ores are in equilibrium.

3.2 RADIONUCLIDES IN PLANT MATERIALS

The major products of the elemental phosphorus industry are elemental phosphorus and the by-products associated with its production. The major by-products are calcium silicate slag produced at rates of 8 to 9 tons per ton of phosphorus produced [6] and ferrophosphorus. Other significant by-products include processed dust removed from furnace offgases and furnace offgas condenser exhaust (CO).

Radionuclide concentrations in elemental phosphorus are very low because of numerous plant production isolation and purification steps. Elevated concentrations of uranium series radionuclides, however, are found in the slag, processed dust, and to a much lesser extent, the ferrophosphorus. An activity balance of the nonvolatile radionuclides entering the production process indicates that most of output activity can be accounted for in the slag.

The elemental phosphorus production process results in the release of fugitive dust and particulate emissions containing uranium series radionuclides. In addition, two long-lived radon daughters, Po-210 and Pb-210, have boiling points low enough to be vaporized by the process, and may be released to the atmosphere. In general, the air pollution control equipment in phosphorus plants is installed to reduce particulate and fluoride emissions. While such equipment is also effective in reducing emissions of radioactive particulate material, it is much less effective at removing radionuclides present as fumes or vapors. Polonium-210, for example, is volatilized during phosphate ore calcining, and significant quantities can be released through particulate emission control equipment during calcining.

3.3 GENERAL INDUSTRY DESCRIPTION

3.3.1 Plants

Table 3-2 lists each plant examined in this study, its location, and its design capacity.

Table 3-2. Domestic Elemental Phosphorus Plants.

Company - Location	Design Capacity ($x10^3$ short tons/yr)
FMC Corporation Pocatello, ID	135
Monsanto Co. Soda Springs, ID	105
Monsanto Co. Columbia, TN	133
Stauffer Chemical Co. Mt. Pleansant, TN	45
Stauffer Chemical Co. Silver Bow, MT	42
Stauffer Chemical Co. Tarpon Springs, FL (Inactive)	23
Occidental Chemical Co. Columbia, TN	50
Mobil Chemical Co. Pierce, FL (Inactive)	20

3.3.2 Basic Process

Elemental phosphorus is produced by a thermal process that uses silica as a fluxing agent for the calcium present in phosphate feed ore. Phosphate is reacted with silica and coke to form elemental phosphorus (P_4), CO, and calcium silicate slag. In addition, by-product ferrophosphorus (FeP) is formed from the reaction of elemental phosphorus with coke and iron oxide. Simplified equations for the process are:

(1) $4\ Ca_5F(PO_4)_3 + 18\ SiO_2 + 30\ C \rightarrow 18\ CaO{\cdot}SiO_2{\cdot}1/9\ CaF_2 + 30\ CO\uparrow + 3P_4\uparrow$
(ore) (slag)

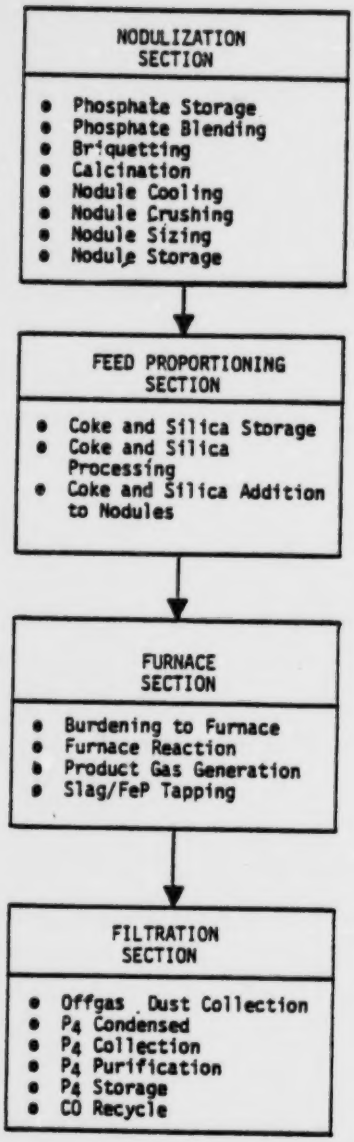
(2) $2\ P_2O_5 + 10\ C \rightarrow 10\ CO\uparrow + P_4\uparrow$ (intermediate reaction)

(3) $2\ Fe_2O_3 + 6C + P_4 \rightarrow 4\ FeP + 6\ CO\uparrow$

A step-by-step diagram of the elemental phosphorus production process is shown in Figure 3-2, and a simplified general process flow diagram is shown in Figure 3-3. The major process steps shown in Figure 3-2 are described below.

- Step 1 -- Phosphate Nodulization. The phosphate feed ore is shipped to the plant and generally stockpiled before use. Various material handling systems are used that blend the phosphate feed ore to achieve required feed specifications. Recycled process fines and dust are typically blended with this phosphate feed ore.

  The blended feed material is sent to a rotary kiln where the material is heated to its incipient melting point (~1300°C) and the tumbling action agglomerates the feed into the desired larger nodular form. In some instances, feed material is briquetted before being sent to calciners that volatize organic material and water, increase P_2O_5 content, and heat-harden the briquettes so they will withstand further processing steps without disintegrating. The nodules or briquettes are then air-cooled and passed through crushing and sizing operations (approximately 1.5-2.5 cm



Step 1

PHOSPHATE FEED NODULIZATION

a. Phosphate is received and stored
b. Nodule/briquette feed is prepared
c. Nodules are formed and calcined
d. Nodules are cooled, crushed and sized
e. Nodules are stored

Step 2

PREPARATION OF FURNACE FEED

a. Coke and silica are received, stored and processed
b. Coke and silica are mixed in proportion with nodules
c. Furnace feed is conveyed to burden bins

Step 3

ELEMENTAL PHOSPHORUS PRODUCTION

a. Furnace feed is fed to furnace
b. Phosphorus is produced
c. CO/P_4 offgas is collected
d. Slag/FeP is tapped and processed or stored

Step 4

ELEMENTAL PHOSPHORUS RECOVERY

a. Dust is removed from furnace offgas
b. P_4 is condensed and collected
c. P_4 is purified and stored
d. CO is recycled to plant or flared

Figure 3-2. Elemental Phosphorus Production Process.

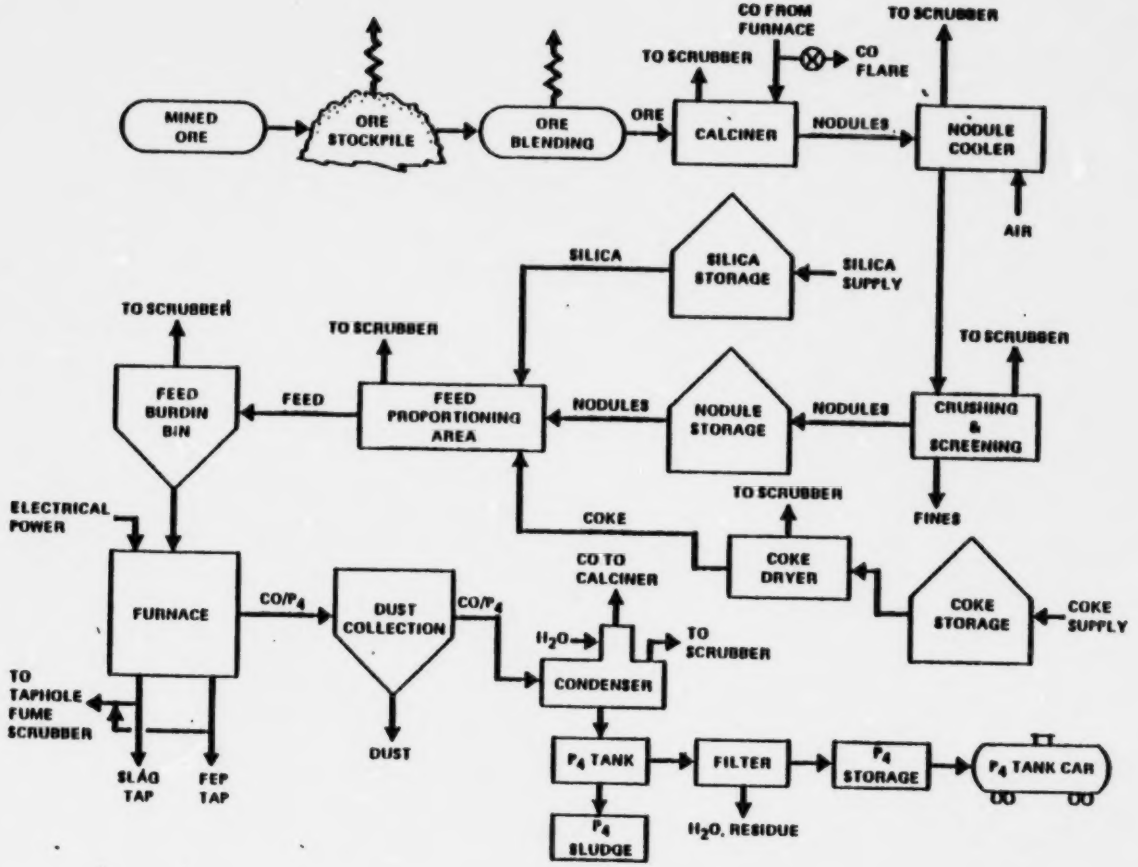


Figure 3-3. General Elemental Phosphorus Plant Process Flow.

diameter) before being sent to storage or to the feed proportioning step of the flowsheet.

- Step 2 -- Furnace Feed Proportioning. The nodulized or briquetted phosphate feed material is sent to a proportioning area where it is mixed with sized coke and silica to obtain the required weight proportion of furnace feed (burden). A proper ratio of SiO_2 to CaO is required to form slag with the necessary flow properties to facilitate removal from the furnace. Coke is added as a carbon source to reduce the intermediate reaction product P_2O_5 to elemental phosphorus. This proportioned furnace feed burden is conveyed to the furnace burden bins.

- Step 3 -- Furnace Operation. The electric furnace is a large chamber lined with carbon blocks in the lower section. Three consumable carbon electrodes extend through the roof to conduct the electric current. An electric arc is formed between the electrodes and the furnace lining. The burden material is gravity fed to the top of the furnace from where it progresses downward until it is heated and eventually melts (at approximately 1400 to 1800°C) in the intense heat of the electric arc. At the heat source, the maximum temperature can reach 4400°C. At 1400 to 1800°C, silica becomes a strong acid that reacts with the calcium phosphate to yield a calcium silicate slag and P_2O_5. The P_2O_5 in turn reacts with the carbon in the coke and is reduced to CO and P_4.

  The elemental phosphorus is driven off as a vapor in the CO off-gas stream. The slag and ferrophosphorus continually collect in the bottom of the furnace in molten layers with the denser ferrophosphorus situated below the slag. Periodically, these molten by-products are separately tapped. Slag is tapped approximately once each hour and ferrophosphorus up to several times each day.

- Step 4 -- Phosphorus Filtration. The furnace product gases are typically treated for dust removal in a mechanical collector or electrostatic precipitator. The cleaned gases are then sent to water spray condensers where the gases are cooled and the phosphorus is condensed to a liquid. Most of the phosphorus-free CO is recycled to fuel the nodulization process. The remaining CO is recycled to other plant operations or exhausted through flare stacks. The condensed phosphorus is collected under water, purified by filtering, and then pumped to underwater storage.

3.3.3 Major Process Variations

The process just described is typical of most elemental phosphorus facilities. However, several major process variations exist among the eight plants examined in this study.

The phosphate ores mined throughout the country possess varying chemical and physical characteristics (e.g., P_2O_5 content and particle size). As a result, each existing plant has its own methods for handling and processing this material before calcination. The various methods used include:

- Crushing, screening, and briquetting
- Drying, screening, and briquetting
- Washing and wet concentrate blending
- Dry blending with other recycle materials

After initial handling and processing, the phosphate feed material is calcined in one of several types of calcining operations. Briquetted feed is typically baked in a moving grate calciner. Generally, phosphate feed is not briquetted but is nodulized during calcination in rotary kilns. Briquetting is currently performed in two of the eight domestic plants and may include the use of phosphoric acid as a binding material. When phosphate feed is calcined in rotary kilns or moving grate calciners, the moisture, sulfur, carbon dioxide, organic matter, and much of the fluorine are volati-

lized. Nodules are typically more porous than uncalcined feeds and result in markedly superior furnace operation as well as decreased power requirements.

The feed proportioning areas of the various plants generally consist of similar operations with a few exceptions. Most plants dry, crush, and screen the coke before mixing it with the phosphate feed nodules. Some plants use significantly different processing and handling procedures. Silica generally undergoes little or no processing other than drying after reaching the plant.

The major process variations in the furnace operation consist of the methods and procedures used to remove and handle slag and ferrophosphorus by-products. Using long probes for flow control, workmen allow molten slag and ferrophosphorus to flow out of the furnace through tapholes. The slag is usually cooled by water spray and then reclaimed for subsequent processing and sale or stockpiling. In some instances, a handling method is used in which a large truck-mounted ladle collects the molten slag, which is then transported to and dumped onto a slag pile where it solidifies. Ferrophosphorus is typically drawn off into chill molds where it is cooled and then processed (crushing and screening) before sale. At some plants, the ferrophosphorus may be removed and sold without processing or may be allowed to flow into trenches with the slag and be subsequently separated after solidification.

Major process variations in the phosphorus filtration section of the flowsheet include the methods and procedures used to remove and process entrained dust in the furnace product offgas stream. Dust is normally removed with a mechanical collector or electrostatic precipitator and then either processed for sale or sent to disposal. Processing methods used consist of fluid bed drying of slurried dust or the use of a burning chamber to treat dry dust. The cleaned furnace offgas stream is normally routed to a spray condenser where phosphorus is separated from the CO. Alternatively, an air-cooled condenser can be used. Condensed phosphorus is collected and then sent to various types of filtering operations to remove impurities. In some instances, phosphorus sludge is treated in roasters or evaporators to increase recovery of phosphorus.

3.3.4 Waste Materials

The major waste streams or materials at elemental phosphorus plants generally consist of:

- Scrubber slurries
- Phossy water (contains phosphorus)
- Dust from collection devices
- Metal or other scrap material

Process streams, such as scrubber slurries and phossy water, are typically sent to on-site settling ponds where the solids are allowed to precipitate. The water is then recovered and usually purified before being recycled to the plant for further use or disposal. Solids in the bottom of the ponds are normally dredged and, depending on their composition, either recycled to the plant or buried on site. At some plants, this material is occasionally sold.

Most dust materials from process collection devices are recycled back to the process. However, some of this material may be sent to on-site disposal (burial). In addition, cleanup fines from some plants are sent to on-site disposal. Scrap metal and other equipment components, such as carbon furnace materials or kiln linings, are either buried on site, stockpiled, or decontaminated and sold.

4.0 STATUS OF COMPLIANCE

Uncertainties in release data can greatly affect any judgment regarding a plant's compliance with the proposed EPA standard of 1 Ci/yr. To provide a better basis of judgment, this section presents available release data and estimates the uncertainties within the data. The factors contributing to uncertainty are identified and quantified, and the ranges of variance for the release estimates are determined. Based on these results, each plant's compliance with the proposed standard is determined. Both out-of-compliance and borderline compliance plants are identified. A plant is defined as being in borderline compliance if its projected release of airborne Po-210, after taking into account the uncertainty associated with such a release, has a reasonable probability of exceeding the proposed EPA standard.

4.1 ASSESSMENT OF PO-210 RELEASES

Two basic methods were used to estimate emissions. Whenever possible, radioanalytical data of samples taken from process streams were gathered and analyzed. Some of these data were published in technical reports or journals, while other data were contained only in company documents or were obtained by private communication. If radionuclide emission data were not available, rates were estimated using emission data from other similar plants for which data were available. The estimated annual emissions are conservative in that they represent the emission rate at full plant design capacity.

A summary of the estimated releases of airborne Po-210 from existing elemental phosphorus plants is given in Table 4-1. For all plants, emissions from the calciners account for either most or virtually all Po-210 emissions. Therefore, detailed uncertainty analyses were performed only for calciner emissions.

Table 4-1. Estimated Airborne Po-210 Emissions From Elemental Phosphorus Plants.

Plant	Total Plant (Ci/yr)	Estimated Releases[1] From Calciner/Kilns (Ci/yr)
FMC - ID	8.2	7.6
Monsanto - ID	3.1	3.0
Monsanto - TN	0.75	0.75
Occidental - TN	0.23	0.23
Stauffer - MT	0.21	0.2
Stauffer - FL	0.17	0.17
Stauffer - TN	0.024	0.023
Mobil Chem - FL	0.019	0.019

(1) Estimated releases may vary from releases quoted elsewhere in this section due to differences in models and methods used to calculate releases and apply uncertainty factors.

4.2 DETERMINATION OF RELEASE UNCERTAINTIES

A number of uncertainties exist both in the data and method used to calculate the estimated releases of Po-210. These include:

- Uncertainties in throughput factors
  - variations in Po-210 concentrations (and parent Pb-210 concentrations) in calciner or kiln feed
  - variations in quantities of ore processed annually
  - variations in ore process rates and percentage operating time between calciner/kilns and between plants
- Uncertainties in data and processes related to stack isokinetic sample collection
  - variations in scrubber efficiencies between calciner stacks and between plants
  - variations, unknowns, and uncertainties in interpreting data related to particulate size distributions
  - variations in exhaust gas flow rates and duct velocity
  - variations in stack gas temperature, pressure, viscosity, and water vapor content (i.e., to correct exhaust flow rates to STP)
  - variations in sampling periods and sample mass collected
- Uncertainties in data and methods related to radioanalytical procedures and analyzed samples

A model was developed to consider these uncertainties. The mathematical formalism in the model is a simplified method of keeping track of the propagation of error from the various parameters affecting the value of the release estimate. It includes the calculations of standard deviations and fractional standard deviations based on the methods discussed in Reference [7].

Despite the effort to quantify all conceivable factors and considerations contributing to uncertainty, a number of uncertainties remain

unquantified. These uncertainties include conflicting information on various plant parameters; the unavailability of sufficient information with which to either interpret or quantify variances in data or perform a complete analysis; the apparent gaps in data in the reviewed literature; and a lack of data and information for some plants needed to resolve issues or parameters of potential significance.

Missing information includes operating details of the phosphorus manufacturing process that could have a significant bearing on the overall uncertainty analysis, including:

- Residence time of volatilized Po-210 between the calciner and the calciner stack outlet

- Method and frequency of recycle of contaminated phossy water and scrubber waste sludge from the settling ponds back to the calciner

- Storage time of waste sludge to permit decay of radioactive Po-210 (half-life = 138 days) to nonhazardous levels

- Amount of uncondensed (and therefore immeasurable) Po-210 as well as the total mass fraction of unsampled particulates that may be lost because of the inability of the isokinetic sampler filter to collect certain particulate sizes

A common practice in elemental phosphorus production is the recycle of phossy water and scrubber waste sludge to the calciner. As this material ultimately contains a significant portion of the volatilized radionuclide, knowledge of the method, frequency, and total residence time of the recycle is crucial to determining the importance of the practice. Some plants recycle only periodically, so that the residence time in recycle varies widely. Others have continuous recycle loops with well-defined residence times. Some plants reclaim the solids in plug flow, others in a well-mixed flow.

All of these factors are important in determining how much Po-210 is returned to the process. If the residence time of the material is short

in comparison to the Po-210 half-life (138 days), then additional recycle of Po-210 must be included in the activity balance of the plant. The data currently available on method and frequency of recycle do not, however, indicate that large amounts of Po-210 are being returned to the kiln.

It is very difficult to determine the physical characteristics (elemental or molecular) of Po-210 as it travels through the plant. Thus, it is uncertain whether all of the Po-210 is attached to the particulates as it enters and subsequently exits the calciner scrubber. The activity balances currently available indicate that the majority of Po-210 emissions are associated with particulate matter. However, because of the uncertainty in such balances, the existence of a molecular species is a possibility and there is limited data to support this possibility. The missing or unknown information collectively could result in more Po-210 in feed material and more Po-210 being released up the stack than is reported.

The following describes the manner in which error analysis was performed. The error model was not developed around existing data but was formulated based on potential areas of uncertainty in stack emissions. Data often had to be manipulated to apply the error model as it now stands, and this manipulation made the model a poor estimator of release. The primary purpose of the error model, however, was to determine uncertainty in an estimate and this was not greatly impacted by the data manipulation. Thus, even though the release estimates derived from this model are not necessarily accurate for the data used in this analysis, the error estimates should be relatively accurate.

Table 4-2 summarizes the error analysis terms used in evaluating FMC emissions uncertainty. The stack activity computation contains assumptions that may be responsible for the release estimate being high. For example, a sample time was inferred from the sample air volume and current sampler flow rates. The actual sampler used, however, may have been unlike those used to determine sample flow rate estimates, yielding a biased result. The remainder of the table uses data with few assumptions and thus has less bias and fewer computational accuracy problems.

Table 4-2. Uncertainty Summary for Po-210 Release from FMC Calciners.

FACTOR	UNITS	ESTIMATE	LOW VALUE	MID VALUE	HIGH VALUE	STANDARD DEVIATION	FRACTIONAL SD, %	2σ UPPER BOUND
Ore Throughput	g/yr	1.49×10^{12}						
#1 Calciner Feed	g/yr		9.139×10^{11}	9.616×10^{11}	1.351×10^{12}	1.947×10^{11}	18.02	2.027×10^{12}
#1 Calciner Avail	-		0.60	0.728	1.00	0.136	20.25	
#2 Calciner Feed	g/yr		8.742×10^{11}	9.457×10^{11}	1.351×10^{12}	2.026×10^{11}	18.68	
#2 Calciner Avail	-		0.74	0.833	1.00	0.084	21.43	
Po Concentration	pCi/g	22.1	17.9	22.1	28.9	3.4	10.02	
Sample Collection EFF	-	1.002					15.38	28.9
R_v - Ratio Velocities	-		0.925	1.0025	1.08	0.1096	23.60	
M_{SR} - Mass Sampled	g/sec		4.797×10^{-6}	5.162×10^{-6}	5.528×10^{-6}	5.169×10^{-7}	10.93	
Stack Activity	pCi/sec	0.2486					10.01	0.3706
Sample Po	pCi/m^3			1700		70	24.54	
Sample Flow Rate	ft^3/min			0.31		0.075	4.12	
Scrubber Efficiency	-						24.19	
Scrubber Eff #1-1[1]	lb/hr		20.9	38.6	57.6	9.5	20.38	
Scrubber Eff #1-2	lb/hr		17.2	25.6	29.4	4.2	24.61	
Scrubber Eff #2-1	lb/hr		18.2	23.3	24.3	2.55	16.41	
Scrubber Eff #2-2	lb/hr		18.3	19.0	22.7	1.85	10.94	
Composite Release	Ci/yr	14.847[2]				4.76	9.70	
							32.08	24.373

(1) First number refers to specific calciner and second number refers to specific stack for that calciner.

(2) Use of model results in emission estimate somewhat higher than actual.

Table 4-2. Uncertainty Summary for Po-210 Release from FMC Calciners. (Continued)

NOTES:

Standard deviation computation in most cases, MAX(HIGH-MID, MID-LOW)/2 = SD

Constants: Sample nozzle area/stack area

sample nozzle	= 3.18×10^{-3} m
stack	= 2.1 m
area correction factor	= 4.375×10^{5}
sec/yr	= 60 sec/min x 60 min/hr x 8760 hr/yr = 3.1536×10^{7} sec/yr
0.0283 m^3	= 1 ft^3

Formulas:

Ore throughput $A_T = C_1T_1 + C_2T_2$ Feed Calciner = C Availability Calciner = T

$$F(A_T) = \left|\left[(C_1T_1)^2 \times (F(C_1)^2 + F(T_1)^2) + (C_2T_2)^2 \times (F(C_2)^2 + F(T_2)^2)\right] / A_T^2\right|^{1/2}$$

Sample Collection Efficiency $M_{SI} = M_{SR} \times \left[K_1 e^{-K_2 R_v}\right]^{-1}$ $K_1 = 3.46$ $K_2 = 1.24$

$$F(M_{SI}) = \left|F(M_{SR})^2 + K_2^2 R_v^2 F(R_v)^2 + 2 K_2 R_v F(M_{SR}) F(R_v)\right|^{1/2}$$

R_v = velocity ratio, M_{SR} = mass rate sampled actual, M_{SI} = mass sampled isokinetic

Stack Activity $S_A = Q \times R \times K$ $K = 4.717 \times 10^{-4}\ m^3 min/ft^3 sec$, Q=sample activity, R=sample flow rate (based on sample of data from FMC)

$$F(S_A) = \left|F(Q)^2 + F(R)^2\right|^{1/2}$$

Composite Release - General form = $S_{AM} \times S_{EFF} \times SC_{EFF} \times P_{CON} \times O_{THR} \times A_{VAIL} \times AREA$

S_{AM}	= ρC_1/sec source from sample	S_{EFF}	= Sample collection efficiency factor
SC_{EFF}	= scrubber efficiency factor	P_{CON}	= Po concentration in ore factor
O_{THR}	= ore throughput factor	A_{VAIL}	= availability - sec/yr
AREA	= constant-area discrepancy		

4.2.1 Mathematical Basis for Determining Uncertainty in Polonium-210 Releases

The annual release of Po-210 from a plant is computed on the basis of many parametric values. The error associated with this release estimate is determined using the release computational formula:

$$Q = \left\{ \sum_{i=1}^{N} W_i \right\} \times P_{7.} \times P_{8.} \qquad (1)$$

$$W_i = K \times P_{1i} \times P_{2i}^{-1} \times P_{3i} \times P_{4i} \times P_{5i} \times P_{6i} \qquad (2)$$

where

Q = Annual release of Po-210 from the plant calciner (curies/yr)

W_i = release of Po-210 from stack i of N stacks over a sample time period (curies/sample time)

P_{1i} = Results of radioanalytical process for sample (curies/sample time)

P_{2i} = Fraction of polonium collected by filter in sample nozzle (dimensionless)

P_{3i} = Variation in flow through sample nozzle versus flow through stack due to changes in stack gas velocity (dimensionless)

P_{4i} = Variation in ore processing rate associated with stack i (dimensionless)

P_{5i} = Variation in efficiency of scrubbers in removing Po-210 in stack i (dimensionless)

P_{6i} = Correction factor to convert stack gas to standard temperature and pressure releases (dimensionless)

$P_{7.}$ = Variation in Po-210 concentration in ore being processed by the plant (dimensionless)

$P_{8.}$ = Number of sample time periods that would represent annual production of plant (sample times/yr)

The dot (.) notation above indicates the lack of the subscript i.

Those parameters representing variations are primarily in the equation as a source of error and should have average values of 1. Thus, for a single stack, the sample analysis will give an estimate in curies for a specific collection time. When divided by the fraction of polonium captured, this value will estimate the Po-210 routed through the sample nozzle. For design conditions, the flow rate through the nozzle versus the flow rate up the stack is known. Thus, a constant multiple, K, of the nozzle Po-210 flow gives the stack flow of Po-210 for the sample time period. The stack flow is corrected to standard temperature and pressure. Variations occur due to stack gas velocity changes (P_{3i}), ore processing rate (P_{4i}), and scrubber efficiency (P_{5i}). To analyze the result, multiple stacks must be summed and multiplied by the number of sample periods in a year considering reduced capacity operation and shutdowns. This value represents the best estimate of the annual release of Po-210 from the plant that can vary with input ore concentration of Po-210 ($P_{7.}$). Note that $P_{7.}$ and $P_{8.}$ are not stack dependent but are plant dependent.

The usual measure of error for numerical parameters is the standard deviation. This discussion will refer to this value as $S(P_{gi})$ where P_{gi} is a general parameter representing P_{1i} through $P_{8.}$ in Equation 2. In error analysis, another measure of error that often simplifies computational formulas and suits the form of data in this particular study is the fractional standard deviation, $F(P_{gi})$. This quantity is stated generally as a percentage and is computed by taking a normal standard deviation and dividing by the average value of the parameter.

Using the formulations discussed in Reference [7], the standard deviation and the fractional SD of the total annual release of Po-210 from a plant are developed. The standard deviation of a function of independent and uncorrelated parameters is found by computing the square root of the sum of the following: partial differentials squared of the function with respect to a parameter times the standard deviation of the parameter squared. Thus, for a calculation of release from only one stack in the plant (N=1), the standard deviation, S(Q), is:

$$S(Q) = \left\{ \sum_{g=1}^{8} \left(\frac{\partial Q}{\partial P_{g.}} \right)^2 \times S(P_{g.})^2 \right\}^{1/2} \qquad (3)$$

This results in a formula for the standard deviation (one sigma) in the following form:

$$\begin{aligned} S(Q) = \Big\{ & \left(K \times P_{2.}^{-1} \times P_{3.} \times P_{4.} \times P_{5.} \times P_{6.} \times P_{7.} \times P_{8.} \right)^2 \times S(P_{1.})^2 + \\ & \left(-K \times P_{1.} \times P_{2.}^{-2} \times P_{3.} \times P_{4.} \times P_{5.} \times P_{6.} \times P_{7.} \times P_{8.} \right)^2 \times S(P_{2.})^2 + \ldots + \\ & \left(K \times P_{1.} \times P_{2.}^{-1} \times P_{3.} \times P_{4.} \times P_{5.} \times P_{6.} \times P_{7.} \right)^2 \times S(P_{8.})^2 \Big\}^{1/2} \end{aligned}$$

Dividing by Q yields the fractional standard deviation, F(Q), which can be converted to the percent uncertainty after multiplying by 100:

$$\begin{aligned} S(Q)/Q = F(Q) &= \left\{ S(P_{1.})^2/P_{1.}^2 + S(P_{2.})^2/P_{2.}^2 + \ldots + S(P_{8.})^2/P_{8.}^2 \right\}^{1/2} \\ &= \left\{ \sum_{g=1}^{8} F(P_{g.})^2 \right\}^{1/2} \qquad (4) \end{aligned}$$

Thus, the square root of the sum of the squares of the fractional standard deviations of the parameters gives the fractional standard deviation for the plant.

When there are multiple stacks in a given plant (N > 1), the formulation is more complex and requires more detailed information. The values of the averages of the parameters must be determined and used as shown below.

$$S(Q) = \left\{ \sum_{g=1}^{6} \sum_{i=1}^{N} \left(\frac{\partial W_i}{\partial P_{gi}} \right)^2 \times P_{7.}^2 \times P_{8.}^2 \times S(P_{gi})^2 + \left(\sum_{i=1}^{N} W_i \right)^2 \times P_{8.}^2 \times S(P_{7.})^2 + \left(\sum_{i=1}^{N} W_i \right)^2 \times P_{7.}^2 \times S(P_{8.})^2 \right\}^{1/2} \quad (5)$$

This results in an equation for the standard deviation of the total plant release:

$$\begin{aligned} S(Q) = \Big\{ & \left(K \times P_{21}^{-1} \times P_{31} \times P_{41} \times P_{51} \times P_{61} \right)^2 \times P_{7.}^2 \times P_{8.}^2 \times S(P_{11})^2 + \ldots + \\ & \left(K \times P_{2N}^{-1} \times P_{3N} \times P_{4N} \times P_{5N} \times P_{6N} \right)^2 \times P_{7.}^2 \times P_{8.}^2 \times S(P_{1N})^2 + \\ & \left(-K \times P_{11} \times P_{21}^{-2} \times P_{31} \times P_{41} \times P_{51} \times P_{61} \right)^2 \times P_{7.}^2 \times P_{8.}^2 \times S(P_{21})^2 + \ldots + \\ & \left(K \times P_{1N} \times P_{2N}^{-1} \times P_{3N} \times P_{4N} \times P_{5N} \right)^2 \times P_{7.}^2 \times P_{8.}^2 \times S(P_{6N})^2 + \\ & \left(\sum_{i=1}^{N} W_i \right)^2 \times P_{8.}^2 \times S(P_{7.})^2 + \left(\sum_{i=1}^{N} W_i \right)^2 \times P_{7.}^2 \times S(P_{8.})^2 \Big\}^{1/2} \end{aligned}$$

Dividing by $Q = \left(\sum_{i=1}^{N} W_i \right) \times P_{7.} \times P_{8.}$ yields

$$F(Q) = \Big\{\Big[\left(K \times P_{21}^{-1} \times P_{31} \times P_{41} \times P_{51} \times P_{61}\right)^2 \times S(P_{11})^2 + \ldots +$$
$$\left(K \times P_{2N}^{-1} \times P_{3N} \times P_{4N} \times P_{5N} \times P_{6N}\right)^2 \times S(P_{1N})^2 +$$
$$\left(K \times P_{11} \times P_{21}^{-2} \times P_{31} \times P_{41} \times P_{51} \times P_{61}\right)^2 \times S(P_{21})^2 + \ldots +$$
$$\left(K \times P_{1N} \times P_{2N}^{-1} \times P_{3N} \times P_{4N} \times P_{5N}\right)^2 \times S(P_{6N})^2\Big] \Big/ \left(\sum_{i=1}^{N} W_i\right)^2 +$$
$$F(P_{7.})^2 + F(P_{8.})^2\Big\}^{1/2}$$

Multiplying the first factor in each term by P_{gi}^2 and dividing the second factor in each term by P_{gi}^2 using the appropriate values of g and i yields the fractional standard deviation or uncertainty factor for the total plant release:

$$F(Q) = \Big\{ \Big[W_1^2 \times F(P_{11})^2 + \ldots + W_N^2 \times F(P_{1N})^2 +$$
$$W_1^2 \times F(P_{21})^2 + \ldots + W_N^2 \times F(P_{6N})^2\Big] \Big/ \left(\sum_{i=1}^{N} W_i\right)^2$$
$$F(P_{7.})^2 + F(P_{8.})^2\Big\}^{1/2}$$

$$= \left\{ \sum_{i=1}^{N} W_i^2 \times \sum_{g=1}^{6} F(P_{gi})^2 \Big/ \left(\sum_{i=1}^{N} W_i\right)^2 + F(P_{7.})^2 + F(P_{8.})^2 \right\}^{1/2} \qquad (6)$$

Thus, if the average values of W_i are known and the fractional standard deviations of the variable parameters, P_{gi}, are known, the error in terms of a fractional standard deviation of annual release can be computed.

4.2.2 Variance in Throughput Factors

Two factors that most importantly characterize the differences between individual plants and site locations are the Po-210 ore concentration (pCi/g) and ore feed rate (g/yr). In addition, the on-stream times for the separate calciners indicates the actual release versus the maximum release potential for a plant assumed operating at 100 percent capacity. The ore concentration of Po-210 and Pb-210 and the known throughput conditions for the various plants are summarized in Table 4-3. Analysis of the uncertainty factors for throughput is solved in two steps.

Table 4-3. Variations in Po-210 and Pb-210 Ore Concentrations and Throughput Conditions.

Plant	Feed Mass Ratios[1]			Radionuclide Concentrations in Feed[1] (pCi/g)					
	Coke	Silica	Ore	Ore		Coke		Silica	
	P_4 Product	P_4 Product	P_4 Product	Pb	Po	Pb	Po	Pb	Po
FMC - ID	1.4[2]	0.8[2]	12.0[2]	27[3]	22[3]	2.4[3]	1.3[3]	0.7[3]	2.6[3]
Stauffer - MT	1.3[2]	1.4[2]	10.1[2]	38[4]	36[4]	0.5[4]	0.3[4]	0.6[4]	2.6
Stauffer - TN	1.6	1.7	10.7	4.2[5]	3.5[5]	0.9[2]	0.8[2]	1.0[2]	0.8[2]
Stauffer - FL	1.2	1.45	9.4	60[5]	59[5]	0.06[2]	0.03[2]	0.08[2]	0.03[2]
Monsanto - TN	1.7	0.2	19.0	4.2[6]	4.1[6]	0.09[6]	0.08[6]	1.0[6]	0.8[6]
Monsanto - ID	1.3	2.6	10.5	27	22	2.4	1.3	0.7	2.6
Mobil Chem - FL	1.4	0.8	13.7	{41 / 49}[2,7]	{49 / 68}[2,7]	1.3	0.8	0.9	0.8
Occidental - TN	1.6	1.7	10.7	4.2	4.1	0.9	0.8	1.0	0.8

(1) Engineering estimates unless otherwise indicated.

(2) Data obtained directly from plant staff - November, 1982.

(3) Data from Reference [8].

(4) Data from Reference [9].

(5) Data from Reference [10].

(6) Data from Reference [11].

(7) Lower values refer to wet ore and higher values refer to dry ore; all ore was assumed to be dry in this study

4.2.2.1 Ore Throughput Uncertainty

For calculating uncertanties in ore throughput, assume that there are two calciners operating with different feed rates and different on-stream times. Therefore, let annual ore throughput be given by the formula:

$$A_T = C_1T_1 + C_2T_2 \tag{7}$$

where

A_T = annual ore thorughput (g/yr)
C_1, C_2 = feed to calciners #1, #2 (g/yr)
T_1, T_2 = on-stream times for calciners #1, #2 (fraction)

The standard deviation is then given by

$$S(A_T) = \left\{ T_1^2 \times S(C_1)^2 + C_1^2 \times S(T_1)^2 + T_2^2 \times S(C_2)^2 + C_2^2 \times S(T_2)^2 \right\}^{1/2} \tag{8}$$

and the fractional standard deviation is given by

$$F(A_T) = \left\{ \left[(C_1T_1)^2 \times \left(F(C_1)^2 + F(T_1)^2 \right) + (C_2T_2)^2 \times \left(F(C_2)^2 + F(T_2)^2 \right) \right] / A_T^2 \right\}^{1/2} \tag{9}$$

The above development of the standard deviation and fractional standard deviation for ore throughput illustrates the application of error propagation analysis. The actual application of the ore throughput uncertainty calculations for the FMC plant is discussed below.

Since FMC has two calciners, as does the error formulation problem just presented, FMC data can be directly substituted. The estimates of throughput of calciners #1 and #2 are 9.616×10^{11} g/yr and 9.457×10^{11} g/yr, respectively. The respective fractional standard deviations are 0.2025 and 0.2143. These four values are substituted for C_1, C_2, $F(C_1)$ and $F(C_2)$ in Equations 7, 8, and 9. Similarly, the availability (on-stream time) of the two calciners is assumed to be 0.728 and 0.833 with uncertanties of 0.1868 and 0.1002. These values are substituted for T_1, T_2, $F(T_1)$, and $F(T_2)$, respectively.

Thus, calciner #1 throughput is computed to be $C_1T_1 = 7.000 \times 10^{11}$ g/yr and calciner #2 has $C_2T_2 = 7.878 \times 10^{11}$ g/yr thoughput. Annual throughput is the sum of these calciner throughputs and is $C_1T_1 + C_2T_2 = A_T = 1.488 \times 10^{12}$ g/yr. The fractional standard deviation for ore throughput $F(A_T)$ is computed to be 0.1802. Note that ore throughput estimates for C_1 and C_2 reflect to some extent the availability of the calciners for the period 1978 through 1981, which was used as a data base. Thus, the uncertainty estimate resulting in this calculation is probably higher than reality. No means of separating throughput estimates from availability factors was found using data at the levels stated above. This introduces a conservatism from the regulatory standpoint into the analysis. However, the conservatism is not thought to be extreme.

4.2.2.2 Calculation of Uncertainty Due to Variation in Ore Concentration

Since only the phosphate ore is used as calciner feed, only the uncertainty in the Po-210 concentration in the phosphate ore need be considered. For the FMC plant, the average Po-210 concentration in phosphate ores is 22.1 $\pm$ 3.4 pCi/g with the standard deviation and fractional standard deviation calculated as:

$$S(P_{con}) = \pm 3.4$$

$$F(P_{con}) = (3.4/22.1) = 0$$

4.2.3 Sample Collection Efficiency

4.2.3.1 General Uncertainty Considerations

Polonium (b p, 960°C) will be substantially volatilized as it leaves a calciner at a temperature of approximately 1300°C. The wet spray scrubber and stack system will, however, typically reduce the exhaust emissions from the stack to a temperature between 50 and 75°C. With sufficient residence time for the exhaust gases to reach equilibrium before leaving the stack, most of the volatilized Po-210 should be condensed onto the exhaust particulates. Assuming this is true, the uncertainty in the polonium emissions sample collection efficiency at the stack is limited to the error in the particulate sample collection efficiency of the EPA's Method 5 isokinetic sampling system (Figure 4-1).

If the exhaust gases have not achieved thermodynamic equilibrium (because stack temperature varies significantly at the sampler location) and a certain fraction of the polonium remains volatilized, estimating the Po-210 emission by collection and radioanalysis of the particulate sample alone may be insufficient and subject to additional uncertainty. The reported input data in Table 4-2 for calculating uncertainties related to sample collection efficiency is based on data from References [8, 11, and 12] which address emissions at the FMC and Monsanto-TN plants. The data in Table 4-4 are only for the calciner stacks at FMC. Each calciner scrubber at the FMC plant has two parallel stacks through which airborne emissions are exhausted.

4.2.3.2 Error in Isokinetic Sampling

Assuming polonium is condensed and plated out on stack particulates, uncertainties associated with sample collection efficiency depend primarily on the ability of the isokinetic EPA Method 5 sampling system to accurately collect representative samples. Unless the velocity of the gas entering the sample nozzle is the same as that velocity of the stream, the sample collected will not be representative of the stream. D.A. Lundgren and S. Calvert [13] have shown that the extent to which the sample is not representative depends primarily on the measure of departure from isokinetic velocity (i.e., the ratio of the sample probe velocity to stack velocity), the size of the particles impacting the nozzle, and to a lesser degree other

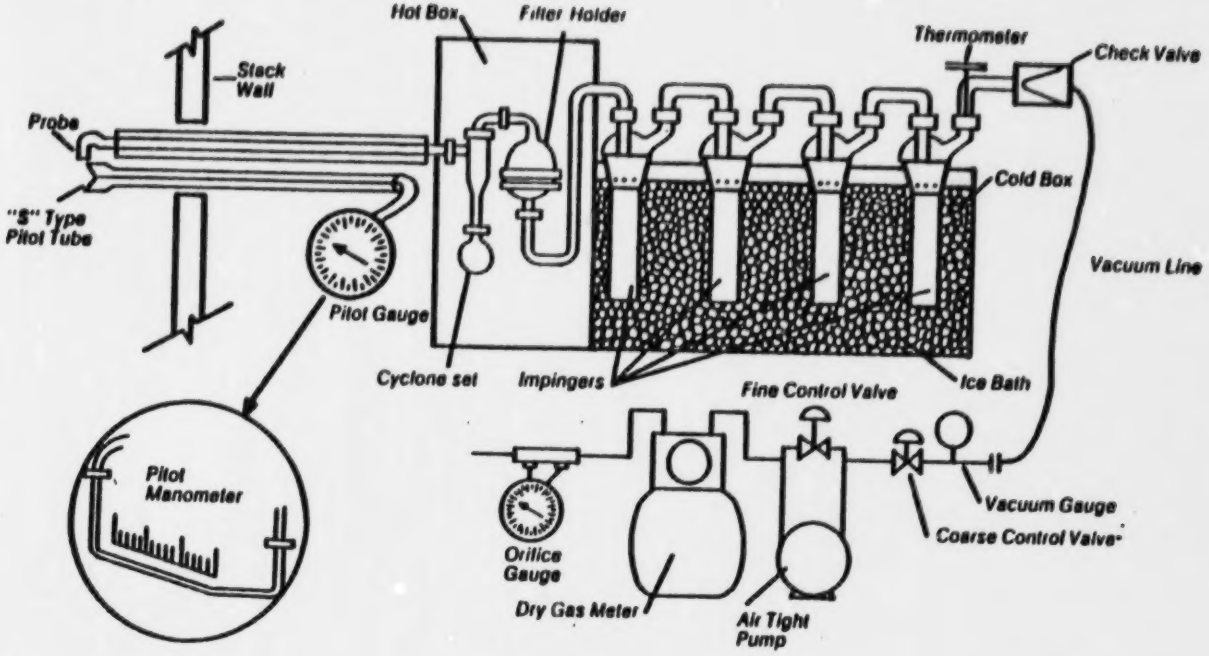


Figure 4-1. Environmental Protection Agency Sampling Train.

Table 4-4. Summary of Estimated Po-210 Releases and Release Uncertainties from FMC Calciner Scrubber Stacks.

Calciner[1] Stack	Mean Value Release (Ci/yr)	Standard[2] Deviation (Ci/yr)	Fractional[2] SD
2-2	2.863	±1.53	0.3679
2-1	3.521	±1.308	0.3714
1-2	3.378	±1.424	0.4216
1-1	5.085	±2.338	0.4097
Total	14.847	±3.211	.2163

(1) First number refers to specific calciner and second number refers to specific stack for that calciner.

(2) Uncertainties do not reflect ore concentration or ore throughput uncertainty.

physical properties of the particles and carrier gas. This error in isokinetic sampling has been represented in the following relationship, which estimates the sampling error for nonisokinetic conditions when using a sharp-edged nozzle facing upstream [14]:

$$\frac{c_s}{c_a} = \frac{(u_a/u_s) - 1}{4\psi + 1} \qquad (10)$$

where

c_s/c_a = ratio of concentration of particles in sample, c_s, to concentration of particles in gas, c_a, (dimensionless fraction)

u_a/u_s = ratio of velocity of gases in stack, u_a, to isokinetic sample velocity at nozzle entrance, u_s (dimensionless fraction)

ψ = inertial impaction parameter equal to $d^2C(\rho_p-\rho)u_a/18\,\mu\,D$

D = diameter of nozzle opening (cm)

d = diameter of particle (cm)

ρ = density of gas (g/cm^3)

ρ_p = density of particles (g/cm^3)

μ = viscosity of gas (poise)

The Cunningham correction factor [15], C, is

$$C = 1.0 + \frac{1.62 \times 10^{-5}}{d} + \frac{0.55 \times 10^{-5}}{d} \exp(-0.67 \times 10^5\, d) \qquad (11)$$

The analysis shows that the error in concentration is less than 20 percent when the velocity ratio, u_a/u_s is between 1/2 and 2 and the inertial impaction parameter is less than 0.1. Because the efficiency varies inversely with particle size, d, the larger the particle size, the greater the error introduced by anisokinetic sampling (see Figure 4-2). Except for d and u_a/u_s, the remainder of the parameters are either constant or are likely to vary to a much lesser degree depending on variations in stack temperature and pressure, For example, the ratio of stack gas densities, ρ_p-ρ, and viscosity, μ, may be expected to vary by the same degree as temperature and pressure vary relative to standard temperature and pressure.

The uncertainty analysis for sample collection efficiency (see Table 4-2) begins by using the results of data provided by the FMC plant to the EPA [12] within the following formula [13] for calculating the percentage isokinetic sampling (ratio of nozzle to stack velocity in Figure 4-2).

$$I = \frac{(V_s/t_s)(T_a/P_a)(P_o/T_o)\ A_s^{-1}C(T_a)^{-1}}{u_a} \times 100$$

$$= (u_s/u_a) \times 100 \qquad (12)$$

The formula is a function of stack flow rate represented by sample volume, V_s, and sample time, t_s; stack temperature, T_a, and stack pressure, P_a, compared with standard temperature, T_o, and standard pressure, P_o; nozzle inlet area, A_s; stack velocity, u_a; and a correction factor, $C(T_a)$, which considers the fluctuation in viscosity of the sample gas as a function of temperature. The stack velocity also varies as a function of temperature and pressure by the relationship

$$u_a = 2.378\left[(P_o/P_a)(28.95/M_g)\ T_a \times R_w\right]^{1/2} \qquad (13)$$

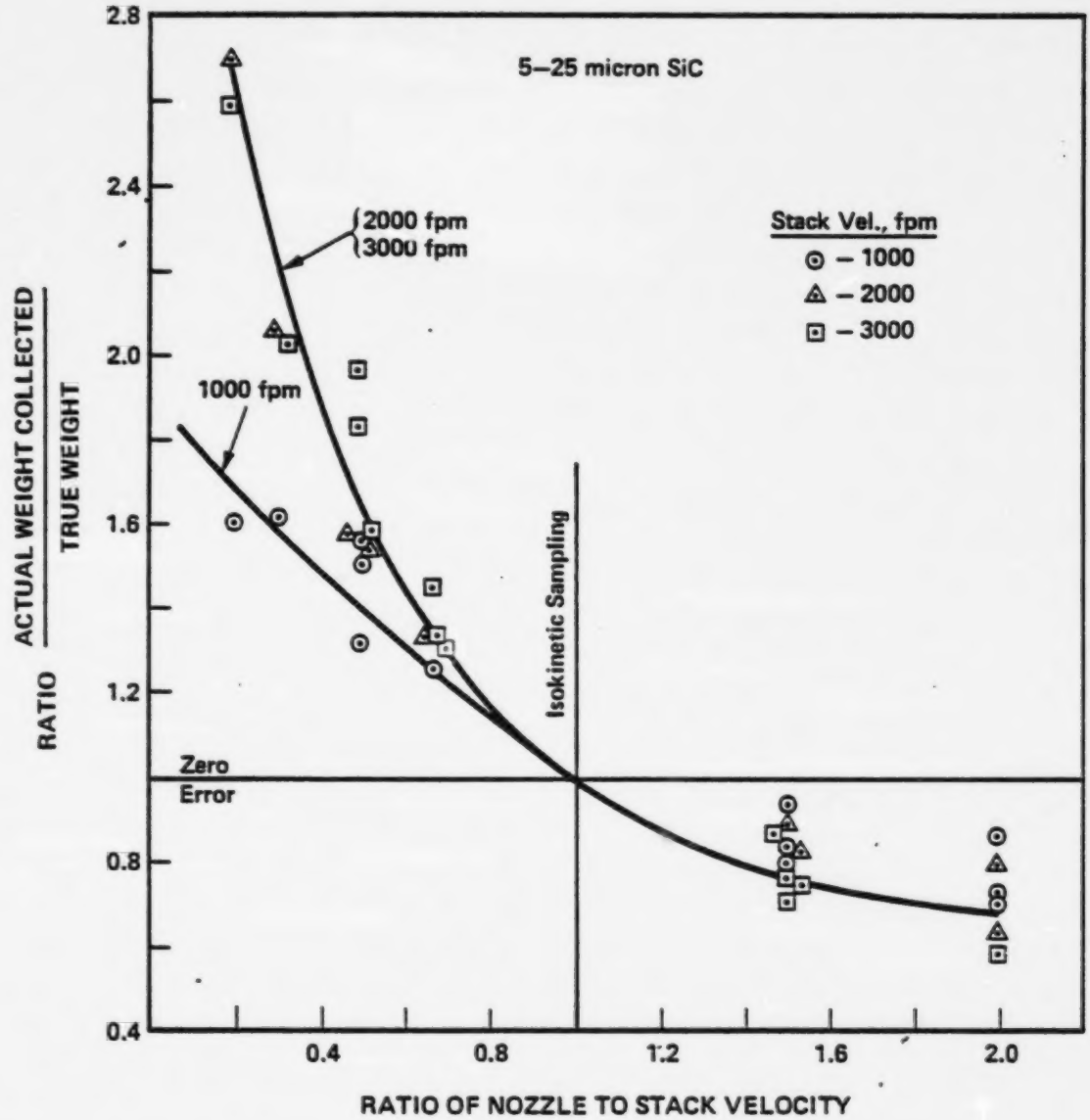


Figure 4-2. Errors Due to Departures From Isokinetic Sampling [16].

where

M_g = molecular weight of the stack gas corrected for standard temperature and pressure (g/mole)

R_w = pitot reading to account for pressure fluctuations as a result of variance in stack flow (dimensionless)

Combining Equations 12 and 13 and dividing by 100 gives R_v, the nozzle to stack velocity ratio used in Figure 4-2:

$$R_v = \frac{K_o(V_s/t_s)}{C(T_a)A_s}\sqrt{\frac{T_a M_g}{P_a R_w}} \qquad (14)$$

where

K_o = 1.857×10^{-2} (dimensionless)
V_s = sampled volume (ft^3)
$C(T_a)$ = viscosity factor = 0.797 to 0.865 in range of temperature considered
t_s = sample collection time (sec)
A_s = sample probe inlet area (ft^2)

The relationship for calculating the relative ratio of stack emissions collected to the true mass of the emissions was fitted from Figure 4-2 and is given by the relationship

$$M_{SI} = M_{SR}[K_1 \exp(-K_2 R_v)]^{-1} \qquad (15)$$

where

M_{SI} = actual stack particulate emissions rate (g/sec)
M_{SR} = mass of sample removed by sampler (g/sec)
R_v = ratio of nozzle to stack velocity, u_s/u_a (dimensionless)
K_1 = 3.46 (dimensionless)

K_2 = 1.24 (dimensionless) (constants K_1,K_2 only apply in the range R_v = 0.8 to 2.0)

The uncertainty analysis is then performed by calculating the standard deviation in terms of errors in the input parameters of Equation 15. Two actual calciner stack samples were used to generate variability data on R_v. The mathematical formulation for the standard deviation is developed in Appendix A.

Because of the variance range on factors such as stack flow rate, temperature, and mass of sample collected and the fact that the exhaust velocity does not typically correspond to the isokinetic sampler design velocity, the overall error in sample collection efficiency is fairly large (24 percent). This uncertainty factor represents the possible error in the emissions release values assuming one fractional standard deviation. The calciner scrubber stack, for example, has a mean calculated sample collection rate of $5.16 \times 10^{-6} \pm 5.169 \times 10^{-7}$ g/sec. Although the mean of the multiplier for sample collection (see Table 4-2) is nearly isokinetic, the error accounting for sample collection efficiency incorporates errors in sample mass as well as the isokinetic sampling fraction and, thus, introduces an error of 24 percent. The error analysis performed for this uncertainty factor assumed full dependence between the ratio of the nozzle to stack velocity, R_v, and the mass rate of collection, M_{SR}.

4.2.4 Radioanalytical Procedures

The primary source of error in radioanalytical sampling procedures is due to the variance in the activity of Po-210 collected on the particulate samples. This analysis in terms of the variance in activity from measurements taken at the #2 calciner and #2 scrubber stack is developed in Appendix A and summarized in Table 4-2. The resulting mean release rate (0.2486 $\pm$ 0.1220 pCi/sec) observed by the isokinetic sampler was based on measurements taken at this calciner stack [8] and using mean estimates of flow rates (adjusted to STP) based on data provided by FMC to EPA during recent sample collection periods [12]. The overall uncertainty for stack activity sample analysis is 0.2454, a factor that contributes significantly to the estimated release from the FMC calciners and the total plant emissions.

4.2.5 Composite Uncertainty Analysis for FMC Calciner

The individual uncertainty factors considered in the foregoing evaluations were combined to give an overall estimate of calciner emissions with a range of uncertainty in terms of a two sigma standard deviation. To calculate the actual release, it was necessary to correct the ratio of the 2.1-m diameter stack area to the 0.318-cm diameter sample nozzle area. This ratio is equal to 4.375×10^5. It was also necessary to account for the number of collection periods and on-stream availability. For 24-hour operation at an estimated 0.833 annual availability (calciner #2-2), the availability correction factor is 2.627×10^7 sec/yr. The availability correction factor has the same uncertainty as the availability (on-stream time) factor ($F(A) = F(T_2) = 0.1002$). Incorporating the scrubber efficiency uncertainty [$F(SC_{EFF}) = 0.097$], the estimated release can be calculated:

$$\text{Release (Ci/yr)} = S_{AM} \times S_{EFF} \times AREA \times SC_{EFF} \times P_{CON} \times O_{THR} \times A_{VAIL}$$

where

S_{AM} = mean value of the Po-210 emissions activity measured by the stack sampler (pCi/sec)

S_{EFF} = mean value of the isokinetic sample collection efficiency (dimensionless)

AREA = constant area correction factor for the calciner stacks = 4.375×10^5 (dimensionless)

SC_{EFF} = correction factor for the mean value of the scrubber efficiency in terms of the amount of material released out of a specified stack to that released from the calciner #2 stack ($SC_{eff} = 1.0$ for calciner #2) (dimensionless)

P_{CON} = correction factor for the ratio of the mean value of the Po-210 concentration in ore feed at a specified plant to that at FMC ($P_{CON} = 1.0$ at FMC)

O_{THR} = correction factor for the ratio of the mean value of ore throughput at a specified plant to that at FMC (O_{THR} = 1.0 at FMC)

A_{VAIL} = availability correction factor (sec/yr)

Using mean values for the FMC calciner #2-2 stack studied, the estimated release was calculated as follows:

$$\text{Estimated Release} = S_{AM} \times S_{EFF} \times AREA \times SC_{EFF} \times P_{CON} \times O_{THR} \times A_{VAIL}$$

$$= 0.2486 \times 1.002 \times 4.375 \times 10^5 \times (1.0)^3 \times 2.627 \times 10^7$$

$$= 2.863 \times 10^{12} \text{ pCi/yr}$$

Fractional standard deviations for each of the respective factors used to calculate the estimated release above are:

$F(S_{AM})$	$F(S_{EFF})$	$F(AREA)$	$F(SC_{EFF})$	$F(P_{CON})$	$F(O_{THR})$	$F(A_{VAIL})$
0.2454	0.2360	0.097	0.0	0.1538	0.1802	0.1002

The above values apply only to calciner stack #2-2 and estimate total release from that stack. Errors for P_{CON} and O_{THR} would be common to other calciner stacks at FMC and are removed from individual stack calculations but included in plant calculations. With modification of the release of Po-210 from the calciner #2-2 stack by appropriate factors based on scrubber emissions from the other calciner scrubber stacks, estimated releases from the other calciner scrubber stacks could be calculated to determine a total plant release (see Table 4-4). The estimated release from the FMC plant with all major sources of uncertainty considered was calculated to be 14.847 $\pm$ 9.526 Ci/yr with a fractional standard deviation of 0.3208 or 32.08 percent. Again, the uncertainty of 32 percent is thought to be relatively accurate but the estimate of 14.8 Ci/yr is thought to be inaccurate due to assumptions made in sample error or stack activity.

4.3 APPLICATION OF UNCERTAINTY FACTORS

Most of the applicable available data used in applying the formalized uncertainty analysis procedure were from the FMC plant. Although the mathematical formulation can be used to determine uncertainty from each stack release at any given plant and then summed for evaluation of total plant releases, this assessment determined detailed uncertainty analyses only for the calciner scrubber stacks. For the FMC plant, these stacks are believed to represent more than 93 percent of the plant emissions. Insufficient data were available on uncertainty parameters for other stacks to warrant detailed uncertainty analysis. In addition, insufficient data were available to permit detailed uncertainty analysis of all parameter groupings at the Monsanto-ID plant, which is also estimated as being out of compliance with the proposed 1 Ci/yr release standard. Thus, the various uncertainty factors calculated for variance conditions at the FMC plant were applied with appropriate multipliers and calculated uncertainty factors regarding throughput at the Monsanto-ID plant to derive expected ranges of release values for the Monsanto-ID plant. Uncertainty factors for the Monsanto-ID plant were based to some degree on data obtained from the Monsanto-TN plant. This same procedure was applied to other plants to obtain a maximum estimated value for Po-210 airborne emissions. The estimated release values and range of uncertainties for each of the eight elemental phosphorus plants is summarized in Table 4-5 and shown graphically in Figure 4-3.

4.4 CLASSIFICATION OF PLANTS

An examination of Table 4-5 and Figure 4-3 shows that the FMC and Monsanto-ID plants are clearly out of compliance with the proposed standard. The FMC emissions are based on what appear to be worst case measurements [8]. More recent sample data [12] tend to indicate that the FMC Po-210 emissions may be closer to the lower bound of the annual emission rate estimates after applying a negative two sigma standard deviation. Even so the plant would still be out of compliance. Maintaining calciner scrubbers at peak operation efficiency may significantly reduce FMC emissions. It should also be reemphasized that these release estimates were calculated in a manner that facilitated the uncertainty estimation. Thus, values were assumed for a number of key parameters affecting release uncertainty, and

Table 4-5. Summary of Polonium-210 Releases from Elemental Phosphorus Plants with Standard Deviations.

Plant	Availability[1] (%)	Annual Release (Ci/yr)	Percentage Error (%)	Standard Deviation (Ci/yr)	2σ Upper Bound Release (Ci/yr)
FMC-ID	78.05	14.847	32.08	4.763	24.373
	100	19.288	31.2	6.028	31.344
Monsanto-TN	78.05	0.583	33.5	0.195	0.974
	100	0.747	30.2	0.226	1.199
Monsanto-ID	78.05	2.471	33.5	0.828	4.127
	100	3.166	30.2	0.957	5.080
Stauffer-MT	78.05	0.156	32.8	0.051	0.258
	100	0.20	30.7	0.061	0.323
Stauffer-TN	78.05	0.018	32.8	0.006	0.030
	100	0.023	30.7	0.007	0.037
Stauffer-FL	78.05	0.133	32.8	0.044	0.220
	100	0.17	30.7	0.052	0.274
Mobil Chem-FL	78.05	0.015	32.8	0.005	0.025
	100	0.019	30.7	0.006	0.031
Occidental-TN	78.05	0.180	32.8	0.059	0.298
	100	0.23	30.7	0.071	0.371

(1) The availability factors shown do not necessarily correspond to current production rates for specific plants.

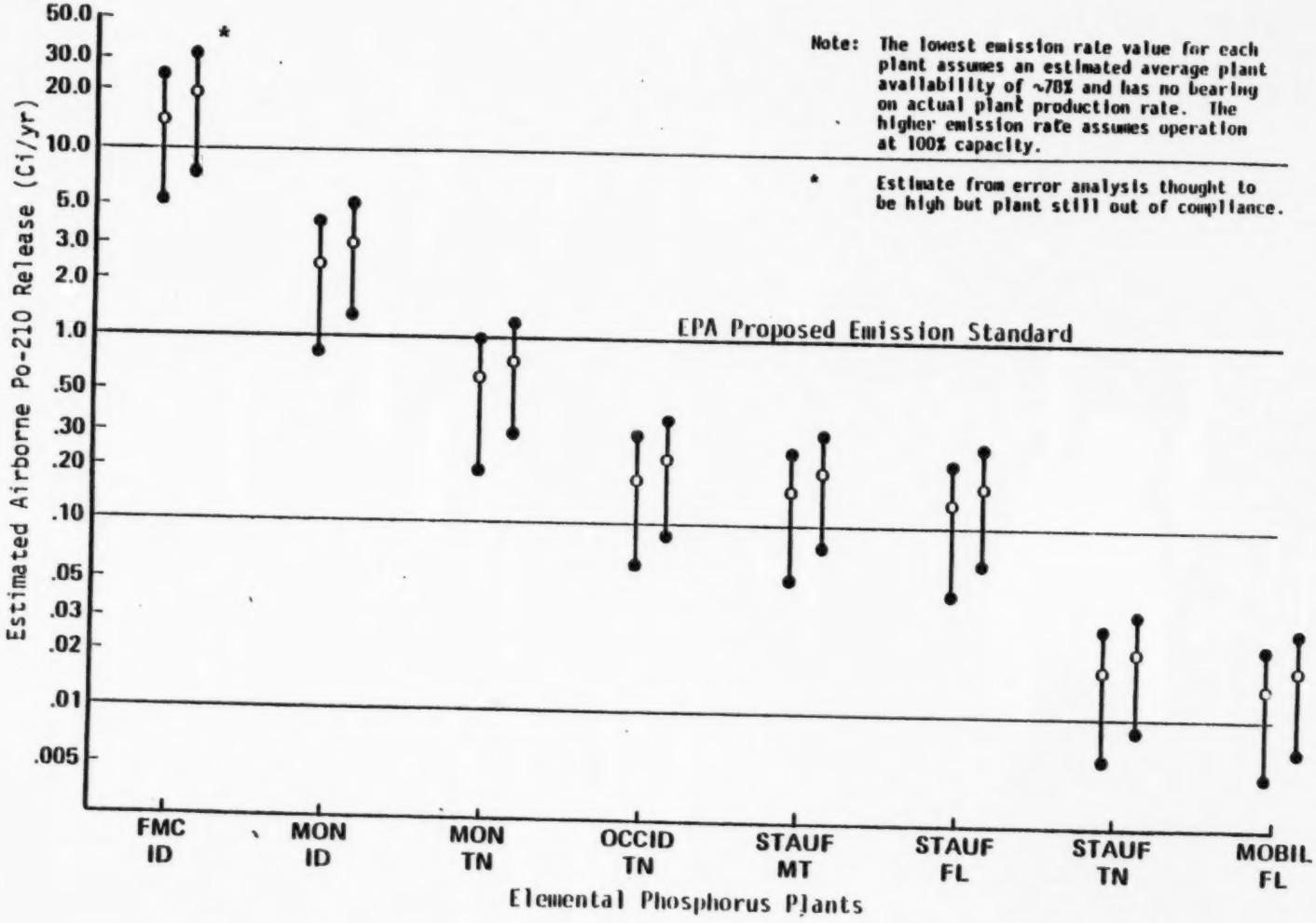


Figure 4-3. Estimated Airborne Po-210 Releases Including Two Sigma Standard Deviation From Elemental Phosphorus Plants.

the release estimates presented here represent those for the particular set of assumed values used in the analysis.

Only one of the eight plants was determined to be in borderline compliance after application of the two sigma standard deviation. The Monsanto-TN plant was estimated to have a maximum release of 1.2 Ci/yr. Because of this and the number of unquantifiable uncertainties due to a general lack of data, the probability of Po-210 emissions exceeding 1 Ci/yr is sufficient to classify this plant as being in borderline compliance.

5.0 POLONIUM CHEMISTRY AND PHYSICAL PROPERTIES

To predict and assess the transport characteristics of polonium through an elemental phosphorus plant, the physical and chemical properties of polonium are required. Because plants have localized conditions of large volumes of high-temperature gas, polonium may first volatilize and then, upon subsequent cooling of the gas stream, condense. Thus, vapor pressure data are important for an engineering assessment of polonium transport. Without a prior knowledge or observations relative to polonium characteristics, however, no specific physical and chemical topics can be eliminated from a literature survey. Therefore, a general review of the physical property data on polonium was required.

5.1 PROBLEMS ASSOCIATED WITH MEASURING POLONIUM CHEMISTRY AND PHYSICAL PROPERTIES

Determining the chemistry and physical properties of polonium and its compounds is very difficult for many reasons. First, polonium is one of the rarest natural elements, with an abundance of only 0.2 percent of that of radium. Uranium ores contain only about 1×10^{-4} grams of polonium per ton [17]. Thus, to make macroscopic physical measurements, polonium-210 must be synthesized in some way, usually by neutron bombardment of natural bismuth. This synthesis, however, is expensive and yields only milligram quantities of polonium. Second, polonium has a very high specific activity. The maximum permissible tolerance for ingested polonium-210 is 2×10^{-8} curies, or 4.5×10^{-12} grams [18]. Thus, exhaustive efforts must be made to ensure the safety of the workers handling the element or its compounds. Expensive equipment, such as glove boxes, vacuum systems, counting equipment, and filter systems, are required. Third, the radiation released by polonium is very destructive to its surroundings. Glassware becomes crazed within days of contact. X-ray capillaries disintegrate or explode in periods of hours

to weeks, and rubber gloves are rapidly penetrated. In addition, the radiation has a self-heating effect on milligram quantities, making accurate weighing of polonium compounds difficult [19].

5.2 LITERATURE SEARCH

To determine what physical and chemical data on polonium and its compounds are available, a literature search was conducted. The bibliography resulting from this search is presented in Appendix B.

The strategy for the literature search was to obtain all articles referenced in chemical abstracts concerning polonium chemistry, polonium physical properties, and polonium transport properties published since 1908. Also, any other papers that appeared useful for determining polonium transport or control in the elemental phosphorus industry were obtained. Several books describing polonium and its chemistry were also found.

5.3 POLONIUM PHYSICAL PROPERTY DATA RELEVANT TO PHOSPHORUS PRODUCTION

Substantial data describing polonium chemistry and physical properties are available, including vapor pressure curves for the pure metal and the dioxide, thermal conductivity, heat capacity, entropy, and thermal output. Qualitative data are also available concerning the reactions of polonium with various elements and the compounds produced by such reactions. The results of theoretical calculations of other physical chemical data have also been published.

The data directly applicable to polonium transport associated with elemental phosphorus production processes, however, are very limited. The vapor pressure curves for polonium and polonium dioxide (which probably indicate a working range of vapor pressures for polonium species) are useful in a qualitative sense. At typical calciner temperatures (1300°C), these compounds have vapor pressures of a few atmospheres [20,21], indicating that polonium will volatilize out of the phosphate ore provided it can reach the solid-gas interface. Most of the remaining data obtained from the literature search was of limited use.

There are no data available concerning the diffusivity and adsorptivity of polonium in porous media. These data are needed to determine how fast polonium will travel through heated ore and how readily it will be adsorbed onto surfaces. In addition, insufficient data concerning polonium

chemistry is available to determine what chemical compounds, if any, are being formed in the process streams at the elemental phosphorus plants. This information would make it possible to predict when and where the polonium will ultimately reside as the temperature of the gas stream decreases. Finally, and perhaps most important, the usual concept of a bulk physical property is not really applicable to polonium during elemental phosphorus production. The amount of polonium in the ore (polonium mole fraction approximately 10^{-8}) and the carbon monoxide process gas (polonium mole fraction approximately 10^{-14}) is so small that accumulations of polonium atoms (or molecules) will probably never exist. For this reason, standard classical thermodynamics and transport phenomena methods related to pure phases will not accurately describe or predict what is happening to polonium.

6.0 BORDERLINE COMPLIANCE PLANT

As shown in Section 3.4, the Monsanto plant in Columbia, Tennessee, is in borderline compliance with the proposed EPA standard. This section discusses the plant and the polonium transport from an engineering perspective, examines the available data, and recommends controls for ensuring compliance.

6.1 ENGINEERING DESCRIPTION OF POLONIUM TRANSPORT

The following description of the Monsanto-TN plant emphasizes polonium transport considerations. The description is based on published data, qualitative information on polonium physical and chemical properties, and information from and conversations with Monsanto personnel.

A simplified engineering process flow diagram with major process and recycle streams is shown in Figure 6-1 for the Monsanto-TN plant. Phosphate ores are roughly blended in a stockpile by layering in one direction and reclaiming at right angles. The reclaimed ore is washed to remove tailings and is then blended with recycled kiln fines and nodule fines before being fed to the kilns. Essentially all the polonium in the ore is fed to the kilns.

The rotary kilns are fueled with coal and carbon monoxide generated in the furnaces. As the temperature of the feed mixture is raised to its sintering temperature (1300^{o}C), it is agglomerated into nodules. Volatilized polonium from this process is swept out with the exhaust gases. The fraction of polonium volatilized is a function of the temperature profiles of the kilns and the size distribution of the agglomerating ore as it travels through the kilns. Because of the relatively fine consistency of the feed ore and the high gas velocities present in the kilns, approximately 25 weight percent of the feed to the kilns is blown out of the process with the exhaust gas [22]. Approximately 80 weight percent of this dust is removed in a high-temperature, ceramic-lined cyclone and recycled to the kiln feed blender. Therefore, approximately 5 weight percent of the feed to

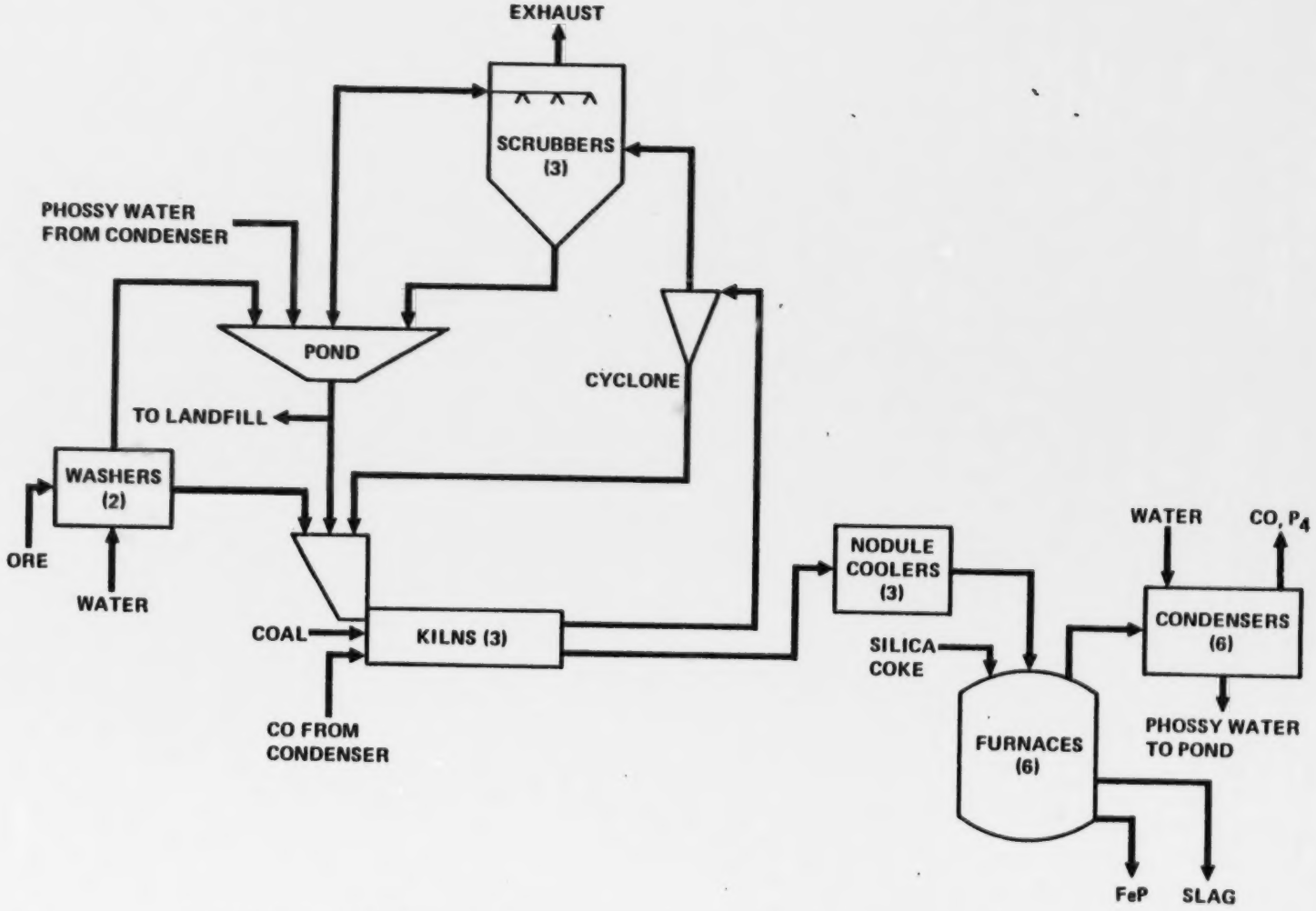


Figure 6-1. Simplified Process Flow Diagram for the Monsanto-TN Plant.

the kilns exits the gas outlet of the cyclone with an estimated 80 percent of the polonium [22].

As the dust-laden stream cools, polonium sorbs onto the available dust surface resulting in an enriched polonium concentration on the relatively fine dust. The polonium is assumed to preferentially condense on finer particles because the fine particles have a greater surface area to mass ratio than the larger particles. This type of enrichment of volatile compounds onto fine particulates has been extensively reported in the open literature [23-27].

Exhaust gases from each kiln cyclone are sent to custom-designed spray tower scrubbers where greater than 89 weight percent of the solids are removed. Scrubber sludge is sent to a settling pond and the clarified water is recycled to the scrubbers. Approximately half of the solids recovered from the pond are recycled to the kilns on an intermittent basis (approximately 1-year residence time). The scrubber exhaust enters the demisting/exhaust stacks tangentially, which improves droplet and mist removal. The cyclonic motion of the gas exiting the exhaust stacks prohibits isokinetic sampling and may induce ingress of air thereby diluting the exhaust gas. Since the polonium apparently concentrates on the fine particulates due to condensation onto the available surface area, the scrubber exhaust contains an estimated 5 to 10 percent of the incoming polonium.

The calcined phosphate nodules leave the kilns with an estimated 20 percent of the incoming polonium. The nodules are cooled, crushed, screened, and stored for future use in feed to the furnaces. The fines from the screening operation (approximately 20 weight percent) are recycled to the kilns.

Phosphate nodules, silica, and coke are fed into electric arc furnaces that reduce the calcined ore to elemental phosphorus, calcium silicate slag, ferrophosphorus (FeP), and CO. The phosphorus is separated from the CO in water spray condensers and is stored for shipment. The CO is pressurized and used as fuel in the kilns. FeP and slag are intermittently tapped and either sold as by-products or stockpiled. A portion of the polonium that enters the furnaces with the feed exits the process in the slag and FeP. The remainder is postulated as leaving with the CO and P_4 gas and either being removed in the water condensers or condensed onto the pipe walls.

The process streams estimated to contain signficant quantities of polonium in the Monsanto-TN elemental phosphorus plant include:

- Feed Materials
  - Ore
  - Coal
  - Silica
  - Coke
- Recycle Streams
  - Kiln cyclone dust (should be minor contributor)
  - Pond solids
  - Nodule fines
  - Phossy water
  - Water tailings
- Intermediate Streams
  - Kiln offgas
  - Scrubber underflow (sludge)
  - Nodules
- Product/Waste/Exhausts Streams
  - Phosphorus (should be minor contributor)
  - Slag
  - Ferrophosphorus
  - Scrubber exhaust gas
  - Pond solids to landfill

The following section elaborates on the data that are the basis of the preceding description.

6.2 QUANTITATIVE EXAMINATION OF POLONIUM MATERIAL BALANCE DATA

The quantitative polonium sample data available for the Monsanto-TN plant are summarized in Tables 6-1 and 6-2 [11,28]. The data shown in Table 6-1 for uranium show an input of 69 to 123 pCi/g P_4 and an output of approximately 90 pCi/g P_4 plus an unknown output in the ore wash tailings

Table 6-1. Estimated Po-210 and U-238 Material Balance for the Monsanto-TN Plant.

Stream	Po-210 (pCi/g P_4)	U-238 (pCi/g P_4)
Inputs		
Ore	92-142	67-121
Coal	1.2	0.5
Silica	0.2	0.6
Coke	1.4	0.7
	95-145	69-123
Outputs		
Kiln scrubber exhaust	3.0-12.4	0.02
Kiln scrubber sludge	98	3.1
Slag	6	83
FeP	0.3	3.3
Phossy water	18	0.6
Ore wash tailings	x(1)	x
	(125-135)+x	90+x

(1) Unknown

Table 6-2. Summary of Relevant Material Balance Data for the Monsanto-TN Plant [11,28].

Stream	Date of Sample	Time of Sample	Po-210 (pCi/g)		U-238 (pCi/g)	
			Average	Range	Average	Range
Tennessee ore	-	-	4.1	2.8-5.3	2.7	2.2-3.2
Florida ore	-	-	59	57-62	43	39-46
Ore tailings	12/14/79	1200	3.6	-	3.1	-
Kiln feed	12/6/79	1000	4.8	4.5-5.0	3.5	3.4-3.5
	12/6/79	1800	7.4	6.4-8.4	6.3	5.8-6.7
Coal	-	-	1.1	-	0.49	-
Kiln scrubber						
Spray water	12/14/79	1200	130 (pCi/l)	-	3.1 (pCi/l)	-
Sludge	12/14/79	1200	1700 (pCi/l)	-	54 (pCi/l)	-
Exhaust	12/6/79[1]	1440	280 (pCi/m^3)	-	0.39 (pCi/m^3)	-
	12/6/79[2]	1820	64 (pCi/m^3)	-	0.43 (pCi/m^3)	-
Nodules	12/6/79	1000	3.3	3.2-3.3	7.5	7.3-7.7
	12/6/79	1000	3.6	2.7-4.5	2.8	2.6-3.0
Silica	12/6/79	1000	<0.8	-	3.2	-
Coke	-	-	<0.8	-	0.42	-
Slag	12/6/79	1400	<0.8	-	11	-
FeP	12/10/79	0920	1.0	-	9.7	8.4-11

(1) 3399 standard m^3/min gas flow.

(2) 3554 standard m^3/min gas flow.

stream. The data for polonium show an input of 95 to 145 pCi/g P_4 and an output of 125 to 135 pCi/g plus an unknown output in the ore wash tailings. In both instances, the results appear quite reasonable from an engineering persepctive.

Data in Table 6-2 must be used only in a qualitative or average sense for several reasons. First, these data were obtained such that concentrations and stream flow rates were not measured at the same time. Thus, estimates of flow rate variations must be made, and these variations are estimated to be on the order of $\pm$10 percent. They are not considered extremely important with respect to overall material balance conclusions. In addition, very few duplicate sample data were taken. Thus, short-term measurement variations and long-term process variations were assumed small since any method of estimating these variations is quite uncertain. Finally, all process streams should be sampled at approximately the same time when the entire process is at steady state operation. It is not known whether plant operations were at steady state when the sample data were obtained.

A possible process upset or variation is illustrated in Table 6-2 by the two kiln feed polonium concentrations taken 8 hours apart measuring 4.8 and 7.4 pCi/g. Statistically, the values are essentially the same in that the values are within the confidence (80 percent) range of each other. However, the two values could have resulted from a varying feed concentration that could affect downstream polonium concentrations. On the other hand, as the polonium feed concentration varied from 4.8 to 7.4 pCi/g, measurements of the polonium concentration in the kiln scrubber exhaust gas stream indicated a range from 280 to 64 pCi/m^3 over approximately the same time span. This appears opposite to the expected result and could indicate a process upset or a highly variable feed concentration of polonium. It would be desirable to know the effect of polonium feed concentrations on polonium kiln scrubber exhaust concentrations so that an understanding of polonium transport could be verified. Based on the average data from Table 6-2, 14.1 Ci/yr of polonium inputted to the kilns would result in approximately 0.75 Ci/yr in the scrubber exhausts.

The data presented in Table 6-2 for the transport of uranium through the kilns must be considered since uranium is not volatile at process temperatures and thus could be considered to be a tracer. The Po-

210/U-238 ratio in two measurements of the calcined nodules is 0.44 and 1.28 compared with feed ratios (before calcining) of 1.17 to 1.37. Since polonium is volatile and uranium is not, the ratio would be expected to decrease after calcining, but the reported ratio of 1.28 does not support this prediction of polonium transport.

Because all available data cannot be explained, only a few specific conclusions can be used in an engineering assessment. Subsequent conclusions drawn with respect to proposed emission controls for polonium at this plant should be viewed in perspective of the available data.

6.3 CONTROL ALTERNATIVES FOR COMPLIANCE

The control procedures that follow are based on the average data presented in the previous section and rely on engineering judgment with respect to estimating the flow of polonium through the phosphorus production processes. The administrative control procedures involve decreasing the polonium flow or diverting an existing flow within the plant. Equipment additions and modifications involve polonium recovery or diverting an existing flow within the plant. The cost estimates for implementing of proposed control alternatives range from insignificant to several million dollars. Since the specific costs of some administrative controls depend greatly upon accounting methods used, only a qualitative description of costs can be given.

6.3.1 Administrative Control Alternatives

Three administrative control alternatives were considered. The first is the limiting or control of polonium (concentration) in the phosphate ore. If polonium input to the calcining process decreased, emissions should decrease even if all the polonium is volatilized. If a fraction of the polonium is volatilized, a constant fraction would probably be volatilized independent of the feed concentration. The polonium material balance data were estimated from sample data apparently taken when a mixture of Tennessee and Florida phosphate ores was fed to the kilns. Since Florida ore has a higher polonium concentration than Tennessee ore, decreasing the amount of Florida ore used would most likely decrease the polonium airborne emission estimate. The Monsanto-TN plant is currently processing only Tennessee ore and so the estimated 0.75 Ci/yr emission may be high and the

plant may actually be in compliance. But since the percentage of Florida ore being used when the sample data were taken is not known, the significance of changing ore sources cannot be fully evaluated. There would be no additional administrative costs associated with continuing to use Tennessee ore as long as it is available. If the ore body is depleted and another source must be used, the relative costs of shipping ore from various locations would have to be compared with estimated polonium emissions.

A second administrative control that might result in decreased emissions is the limiting or cessation of recycling pond sludge. Intermittently, about half of the pond sludge is recycled to the kiln feed system. Recycle after approximately a 1-year residence time results in approximately a 7 percent increase in airborne polonium emissions from the kiln scrubbers. Without recycle of sludge, airborne polonium emissions would be minimized because less polonium would enter the process. The costs of limiting or stopping sludge recycle are those associated with disposal and use of additional phosphate ore. Since approximately one-half of the sludge is currently disposed of, the estimated costs for this control alternative are expected to be relatively minor.

The final administrative control alternative considered is limiting elemental phosphorus production rate to the point where only 1 Ci/yr of polonium is released. This alternative would cost at least as much as the cost of performing analytical measurements on the scrubber stacks for a year. Each analysis is estimated to cost no more than $1000, so that weekly analysis would cost approximately $52,000 per year. If the cumulative polonium emissions exceeded 1 Ci before the end of the year, the plant could be shut down to ensure compliance. But since much of the phosphorus produced at this plant is used as raw material at other Monsanto chemical plants, elemental phosphorus would have to be purchased to make up for decreased production. The immediate cost incurred would be the cost differential between the outside purchase and the internal production. This cost differential would be highly dependent upon supply and demand and would fluctuate accordingly.

6.3.2 Equipment Control Alternatives

Equipment modifications proposed to control airborne polonium emissions to 1 Ci/yr include modifying the ore processing method upstream of the kilns and adding conventional particulate control equipment to the gas exhaust streams from the kiln scrubbers. The proposed modification to the ore processing procedure used in preparing kiln feed is to pelletize or briquette the ore before calcining. By pelletizing some or all the ore, much of the polonium would reside in a relatively large solid matrix. When subjected to high temperatures during calcination, polonium would have to be transported through the solid material a much longer average distance to escape into the kiln atmosphere. This appears to occur at the FMC plant where briquetting of the feed is practiced and a substantial fraction of the polonium is retained in the calcined briquettes. The amount of polonium volatilized would be subject to variation in kiln operating procedures and conditions.

The potential success of this control alternative depends upon the size distribution of the fine particulates generated during calcining of the pellets. Potentially smaller particulates than those produced during conventional operation might be blown out of the kiln resulting in more polonium condensing on these particulates. In this instance, less polonium might be volatilized in the kilns but more polonium might condense on the finer particulates and so the emission rate may not change. The cost of implementing ore pelletizing depends on the amount of ore pelletized and to some extent the size of the pellets [29].

Polonium retained in the briquettes would not be ultimately recycled to the kiln with CO as a result of voltilization in the high-temperature furnaces. Furnace offgas CO is routed through water condensers to recover elemental phosphorus. Any polonium in the CO stream would be expected to condense. However, there is essentially no polonium in the phosphorus product.

The second equipment alternative is the recovery of fine particulates from a portion of the scrubber exhaust stream(s). To reduce emissions to 1 Ci/yr, the entire exhaust stream from each kiln scrubber would have to be processed. Particulate control equipment such as a baghouse or an electrostatic precipitator (ESP) would remove approximately 95 to 98 percent of the 0.1 to 1.0 micron diameter particulates in the process stream(s)

(see Chapter 7 for discussion of these operations). An order-of-magnitude capital cost for either a baghouse or an ESP is 2 to 10 million dollars depending on the fractions of the exhaust stream processed. This capital cost is an installed cost and will yield a unit ready for operation.

7.0 PLANTS OUT OF COMPLIANCE

7.1 ENGINEERING DESCRIPTION OF POLONIUM TRANSPORT

As shown in Section 4, the FMC and Monsanto-ID elemental phosphorus plants were determined to be out of compliance. The following sections describe polonium transport from an engineering perspective for these two out-of-compliance plants. Data are at times somewhat limited and even contradictory. The reasons the data cannot always be explained may be due to inaccuracy or a lack of understanding of the physical chemistry of polonium. Potential equipment for controlling emissions is then evaluated in light of the transport phenomena. Costs are estimated for each viable control alternative.

7.1.1 FMC Process

The FMC calcining process is essentially a once-through process with no recycle of polonium-bearing material as illustrated by an estimated polonium material balance shown in Figure 7-1 [30]. The polonium entering either of two calciners results from the natural decay of uranium in the parent ore. As the result of a feed briquetting operation, the high-temperature calciners do not volatilize all the polonium. Briquetting of the feed produces a solid structure that contains the polonium. Thus, for polonium to volatilize to the calciner atmosphere, it must be transported from the bulk interior of the briquettes to the surface. The calciners are of a traveling grate design whereby a bin of briquettes is continuously pulled through a heating chamber. Briquette temperatures during this process reach 1260^{o}C at the top of the bin with lower temperatures at the bottom. This is in contrast to a nodulizing kiln operation where ore is fed directly to a kiln and the nodules (similar to briquettes) agglomerate at a temperature high enough to promote sintering (approximately 1300^{o}C). During nodulizing, the polonium is volatilized before a relatively solid matrix is produced,

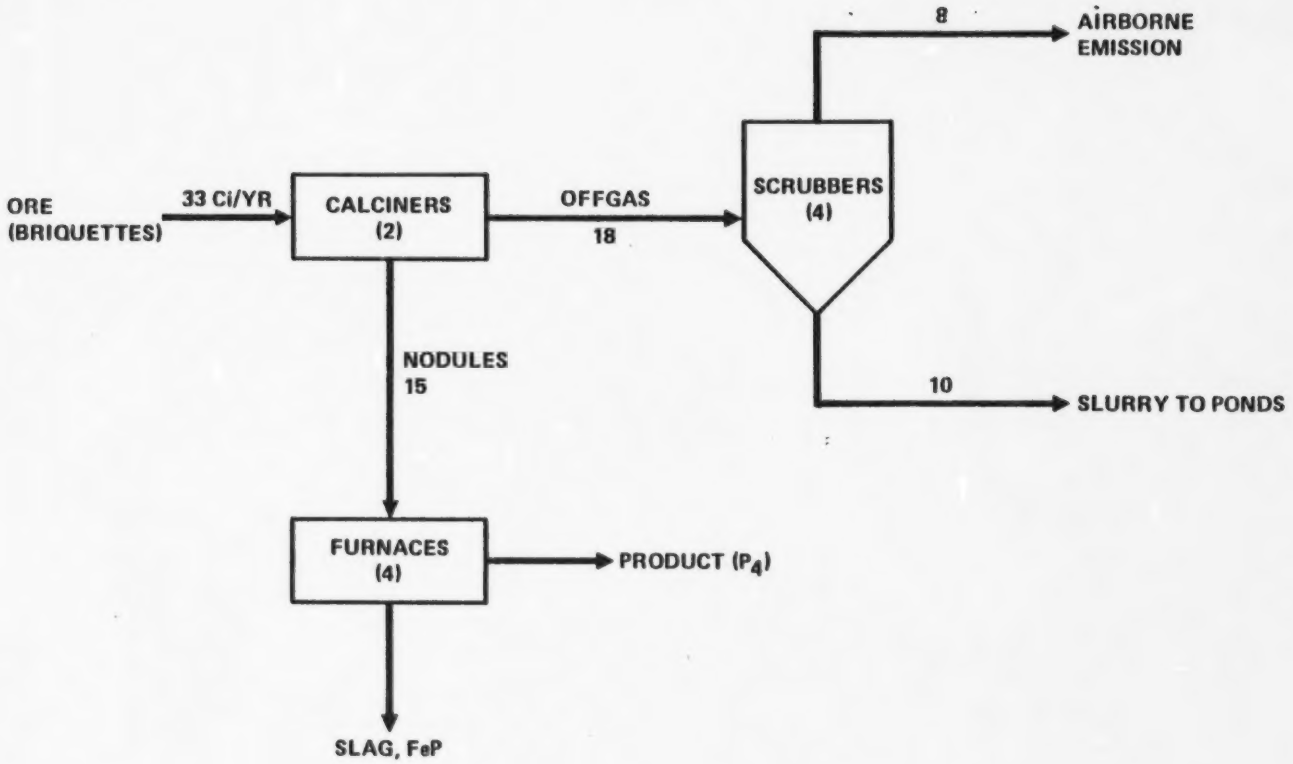


Figure 7-1. Simplified Process Flow Diagram and Po-210 Balance for the FMC Plant.

and so the radionuclide does not have to be transported from the interior of a relatively large solid to its surface.

The briquetting operation and subsequent high-temperature calcining of the briquettes at the FMC plant volatilize approximately 18 Ci/year of polonium out of the 33 Ci/year in the feed. The solids loading in the calciner exhaust gas provides surface area for polonium condensation as this gas cools. The solids loading in the calciner gas is relatively low compared with that in nodulizing operations, and the particle size distribution is relatively fine. These characteristics exist because the briquettes are carried through the calciners rather than tumbled through. Thus, there is no attrition of solids to produce a relatively high particle loading in the gas or a particle size distribution with a larger fraction of coarse material.

The solids and volatilized polonium in the gas from each calciner are routed to two disc scrubbers. Atmospheric inleakage cools this gas to approximately 260 to 320^{o}C. The gas is then quenched in the scrubbers where the polonium is likely to condense on the surface of the particles in the gas. Since the particle size distribution is characterized by particulates on the order of 0.5 microns in diameter and less, the efficiencies of the disc scrubbers are expected to be significantly less than 90 percent. Most wet scrubbing devices attain high efficiencies (98 percent) for particles larger than 2 to 3 microns, intermediate efficiencies (50 percent) for particles in the 1 to 3 micron range, and much lower efficiencies for particles less than 1 micron in diameter. While these particle size efficiencies are general, significantly better wet scrubber efficiencies do not appear to be attainable.

The polonium balance around the FMC disc scrubbers indicates that the polonium recovery efficiency is approximately 50 percent. The polonium is assumed to preferentially condense on finer particles because the fine particles have a greater surface area to mass ratio than the larger particles. Thus, while the polonium recovery efficiency of the disc scrubbers appears to be approximately 50 percent, this should not be interpreted as a particle mass recovery efficiency.

To reduce airborne polonium emissions from 8 to 1 Ci/yr, the mass particle recovery efficiency must be on the order of 90 percent for all particles below the 2 to 3 micron range. A grade efficiency, or recovery

efficiency versus particle size, for a particle recovery unit operation cannot be specified without more information about the partitioning of polonium versus particle size. Since the particles generated in the FMC calcining process are not expected to be spherical, surface area versus size is not known. To provide a margin of safety, the design criterion for a particle recovery device must be a recovery efficiency of 95 to 98 percent for all particle sizes in the 0.1 to 1 micron range.

Another possibility which might account for the atmospheric release of polonium from the FMC disc scrubbers is that the polonium may not totally condense onto surfaces in the scrubbers. Thus, a gaseous species transports through the scrubber. This possibility seems remote because a material balance of the Mobil Chemical elemental phosphorus plant indicates polonium does not volatilize at 175°C [31], and the disc scrubbers at FMC are at ambient temperature.

There is very little evidence available to verify the engineering description of polonium transport in the FMC process as described here. Clearly, the most important data to verify the engineering description are material balances around the disc scrubbers. These material balances must include all streams such as the solids discharge from the scrubber for nonvolatile species such as uranium. For uranium recovery in the scrubbers, a recovery efficiency matching that of the particulate recovery on a mass basis is expected. The polonium recovery efficiencies of the disc scrubbers indicate the particulate surface-area recovery efficiency of the device.

7.1.2 Monsanto-ID Process

The calcining operation at the Monsanto-ID plant includes a rotary kiln with recycle of kiln offgas scrubber underflow. An estimated polonium material balance for the kiln operation is shown in Figure 7-2 [32]. The polonium entering the kiln results from natural decay of uranium in the parent ore. As the ore is heated and tumbled in the kiln, approximately 90 to 95 percent of the polonium is volatilized and leaves the kiln in the gas phase. This is because polonium has a high vapor pressure (a few atmospheres) at kiln temperature (approximately 1300°C) and must travel a relatively small distance through the ore to reach the gas-solid interface.

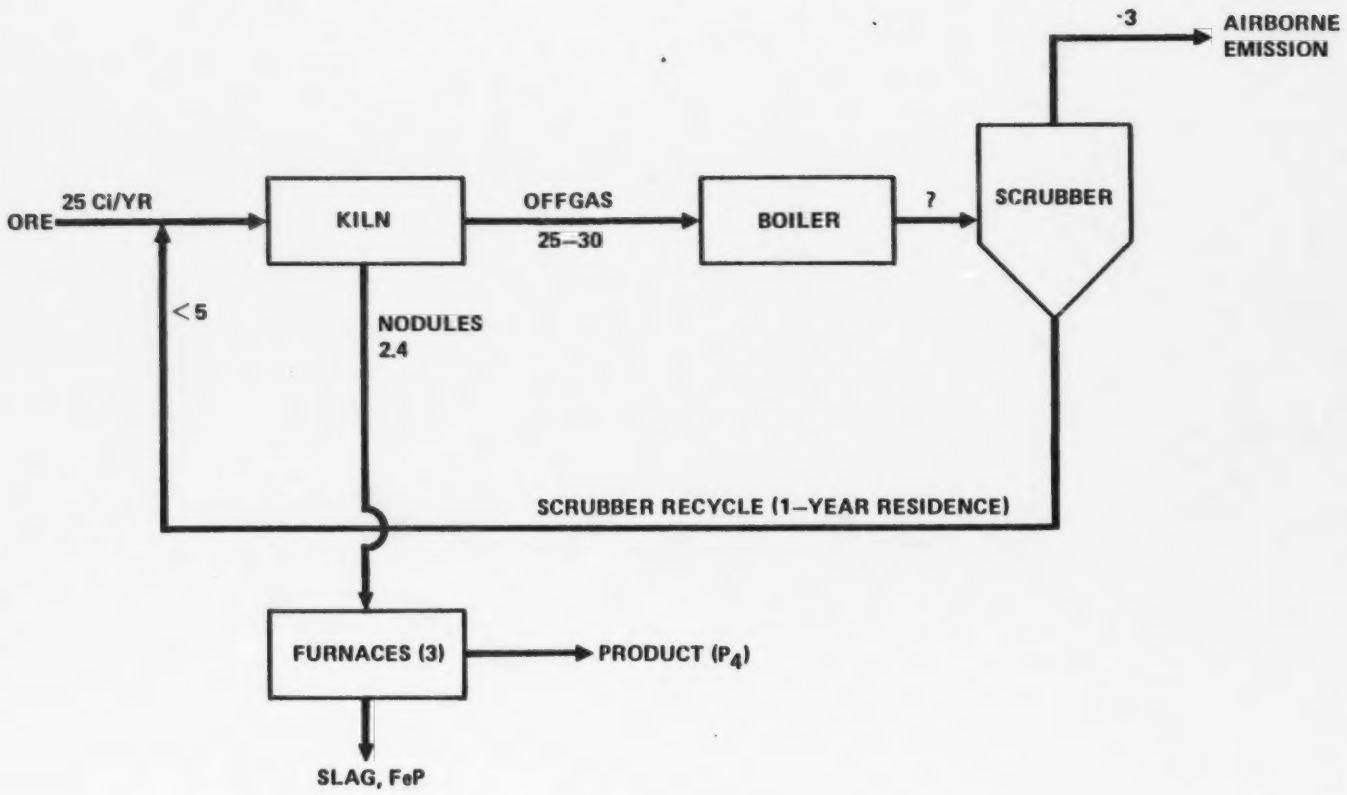


Figure 7-2. Simplified Process Flow Diagram and Po-210 Balance For the Monsanto-ID Plant.

This is in contrast to plants using briquettes where mass transport of polonium must occur over a much longer distance.

The same gas stream that carries the polonium out of the kiln also sweeps out particulates. Typically, about 20 weight percent of the kiln feed is blown out in this manner. An approximate particle size distribution [32] for this gas stream is

Particle Diameter (μm)	Cumulative Percent Less Than Stated Size
1.0	25
2.0	35
3.0	45
5.0	85
10.0	95
25.0	100

This gas stream is treated by a series of emission control equipment items including a knockout chamber, a boiler, a spray tower, and a demister. The knockout chamber has an efficiency of approximately 10 weight percent and is designed to remove the very large particles (>20 micron). The boiler is designed to recover some of the heat produced in the kiln. The spray tower is designed to remove particulates and flouride from the gas stream. The collective particle removal efficiency for these devices is approximately 99.9 weight percent. The majority of these particles are removed in the spray tower in the form of an underflow slurry, which is sent to a series of settling ponds. In these ponds, the scrubber water is separated from the solids and recycled. The solids are piled to dry and then continuously recycled to the kiln in plug flow. The residence time for the solids in this cycle is approximately one year.

A complete mass or activity balance for polonium cannot be completed at this time. Some activity measurements are available in the feed ore and in the nodules. However, activity data from stack emissions, boiler surfaces, scrubber slurry, CO gas recycle, drying ponds, and other important process locations are not available.

The Monsanto-ID plant has been estimated to be out of compliance based upon data from other similar plants, corrected for differences in ore activity and total production rate. This method of estimation is only a starting point. As will be discussed below, there are subtle but perhaps very important differences between the Monsanto-ID plant and the plants used to make the estimates. Although the current understanding of polonium transport through the plant is discussed below, actual activity measurements of the process streams at the plant would be required to verify the accuracy of that understanding.

The annual amount of polonium in the ore entering the plant is estimated to be approximately 25 Ci. The polonium activity fed to the kiln is approximately 25 Ci/yr plus whatever is recycled from the knockout chamber and spray tower (probably less than 5 Ci/yr). Since an estimated 2.4 Ci/yr leave the kiln with the nodules, 25 to 30 Ci/yr leave the kiln in the gas stream. To meet the proposed standard of 1 Ci/yr, the combined polonium removal efficiency for the knockout chamber, boiler, spray tower, and demister must be at least 96 to 97 percent. To provide a margin of safety, an efficiency of 98 to 99 percent should be achieved.

The physical state and location of the polonium as it leaves the kiln and travels through the control equipment is very dependent upon time and temperature. As the temperature of the gas stream decreases from 1300°C in the kiln to 60° C in the stack, the vapor pressure of the polonium drops and polonium condenses on a surface. The available surfaces include the particulates, the walls of the ducting, the boiler tubes, and the stack walls. Without pertinent physical property data, determination of the locations at which this happens is very difficult.

If it is assumed that the polonium in the gas stream remains in approximate thermal equilibrium, the temperature drop in the boiler would cause the polonium to condense on the boiler tubes and on the particulates. However, since the residence time in the boiler is short, some polonium may remain in the gas phase past the boiler and condense onto the particulates after it arrives in the spray tower, where the temperature is further reduced.

Because of a scarcity of data for the Monsanto-ID plant, Monsanto-TN plant data were used as a basis to estimate the emissions from the Monsanto-ID plant. The Tennessee plant, however, does not use a boiler to

recover heat from the kiln offgas. This process difference appears small, but the boiler could remove a significant amount of polonium from the gas stream. The effect of the boiler on the estimated polonium balance cannot be assessed without more information.

If the estimated kiln scrubber stack emission value of 3 Ci/yr is accurate, then the current overall polonium removal efficiency is approximately 90 percent. The engineering task would then be to increase this efficiency to 98 to 99 percent to achieve compliance.

The particle size distribution for Monsanto-ID indicates that 25 weight percent of the particles are less than or equal to 1.0 micron in diameter. Therefore, more than 25 percent of the polonium should be distributed on these small particles, and a design criterion for compliance would be 98 to 99 percent removal of all submicron particles. An exact polonium distribution is impossible to calculate because the relationship between surface area and particle size is not known.

7.2 FINE PARTICULATE CONTROL

As just discussed, FMC and Monsanto-ID must control between 95 and 99 weight percent of all particulates between 0.1 and 1.0 micron. The recovery of fine particulates, generally considered to mean particulates with diameters less than 2 microns [33,34], is somewhat more difficult than recovery of larger particulates. Virtually all particulate recovery unit operations have lower relative recovery efficiencies in the critical 0.1 to 1.0 micron particle diameter region than in other regions. Some of these operations may even exhibit improved recovery efficiencies below 0.1 micron.

The recovery of fine particulates from a gas stream involves the collection of those particulates on a surface. Thus, the particulate must somehow contact the collection surface. The principal mechanisms of particulate recovery are inertial impaction, interception, diffusion, and motion in an applied electric field (or other field gradient). These mechanisms have been studied extensively and reported in the open literature and are the subjects of many research topics.

Most particulate collection units exhibit minima in collection efficiency with respect to particulate size. A minimum has been shown to exist both theoretically [35] and in actual practice for barrier filters [36]. The theory of particle collection in electrostatic precipitators is

considerably more complicated than that for a barrier filter, but the theory predicts a minimum in particle collection in the region of 0.1 to 0.5 micron [37]. The other major unit for particulate recovery is a wet scrubber. The types of scrubber found in industrial use range from spray towers to high-energy wet venturi scrubbers. The theoretical design equations for venturi scrubbers do not show a minimum in particle collection efficiency in the 0.1 to 1.0 micron region because the design equations are based on the inertial impaction collection mechanism only [38]. This mechanism becomes less effective with decreasing particle size in the region of 1.0 micron particle diameter.

The following sections evaluate barrier filters, electrostatic precipitators, venturi scrubbers and novel collectors in relation to the FMC and Monsanto-ID plants.

7.2.1 Barrier Filtration

Barrier filtration is the removal of particles from a flowing stream by action of a stationary filter medium. The filter medium can be a dry fabric such as a bag filter, a wet fabric or packing such as a demister, or a rigid dry filter such as a porous metal. Examples of dry fabric filter efficiencies are presented in Table 7-1 [39]. These efficiencies must not be interpreted as being attainable for all situations. Extrapolation of this data is risky because filtration efficiency will be affected by the entire particulate size distribution. A portion of the filtered particulate will always remain on the filter after the cleaning process, and these retained particles aid and affect the particulate recovery efficiency. The recovery of 0.1 to 1.0 micron diameter particulates is expected to be the same for two filter systems only when the particulate size distributions are identical. For process design for polonium recovery at the Monsanto-ID and FMC calciner operations, a Nomex baghouse filter system with an air-to-cloth ratio of 4 has been considered.

Another possible barrier filter is a wetted mat, an industrial version of which is the Cleanable Media High Efficiency Air Filter (CHEAF) system [40]. The typical operating performance indicates, however, the likelihood that this filtration system would probably not satisfy the process design criterion of a particle recovery efficiency of 95 to 98 percent for 0.1 to 1.0 micron diameter particles. Test data for a phosphorus

Table 7-1. Collection Efficiency of Fabric Filters [39].

Filter Fabric & Cleaning Type	Air-to-Cloth Ratio(1)	Efficiency At Particle Diameter, %		
		1 μm	0.5 μm	<0.3 μm
Glass/teflon reverse air	2	99.7	99.8	94.5
Nomex reverse air	~3	99.6	99.2	99.9
Glass/graphite repressure air plus shaker	~4	98.3	98.9	98+

(1) Air-to-cloth ratio normally expressed in cfm gas flow per ft^2 filter area.

furnace taphole fume stream where 28 percent of the particles were less than 0.5 micron and 92 cumulative percent were less than 1 micron showed an overall (entire distribution) collection efficiency of 96 percent [40]. Thus, the collection efficiency for 0.5 micron particles would probably be less than 96 percent. A review of advanced techniques for fine particulate control [39] rated the CHEAF system particle recovery efficiency for 0.5 micron particulates at approximately 95 percent. Hence, a wetted-mat filtration system was not considered for calciner emission control at the Monsanto-ID and FMC plants.

7.2.2 Electrostatic Precipitators

The detailed design of an electrostatic precipitator requires considerable information about the particulates to be recovered. The performance-related parameters include gas flow, temperature and velocity, specific collection area, overall particle mass collection efficiency, fractional (grade) efficiency, inlet and outlet solids loading, and chemical analysis of the particulate [41]. To size an electrostatic precipitator for a given design criterion on a phosphorus ore calciner exhaust gas stream, more data are required. In spite of considerable research carried out to understand the mechanisms and theory behind electrostatic precipitation, the theory is of little use in the final design of a commercial precipitator [42]. Therefore, a general overview on electrostatic precipitator performance and short-cut design methods were used in the current study.

Most of the electrostatic precipitator performance data reported is from coal-fired power plants. Examples of particulate recovery efficiencies as a function of particle size are presented in Figures 7-3 and 7-4 [37]. The important characteristic of these efficiency curves is that the efficiencies around a particle diameter of 0.5 micron are approximately 95 to 98 percent. If the same performance can be attained for the Monsanto-ID and FMC calciner exhaust streams, it is reasonable to expect that the standard of 1 Ci/year of polonium release could be met. However, extrapolating performance as indicated here is not recommended, and detailed design would have to be conducted to finalize any management and regulatory decisions.

The ESP unit must be sized before costs can be estimated. Using the simplified method in Reference [43], a size of 0.79 m^2 of collecting

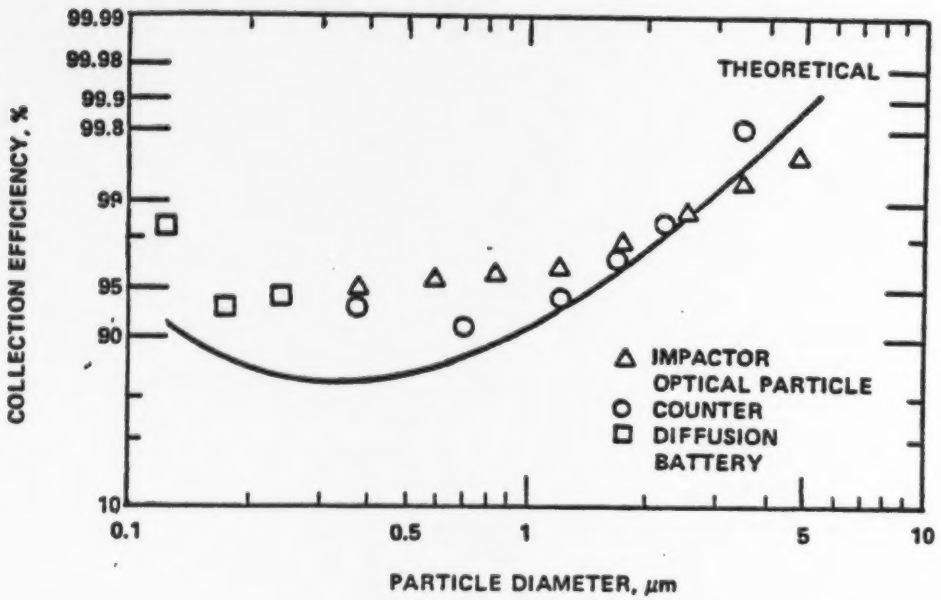


Figure 7-3. Measured and Computed Efficiency as a Function of Particle Size for an Electrostatic Precipitator at A Coal-Burning Power Plant [37].

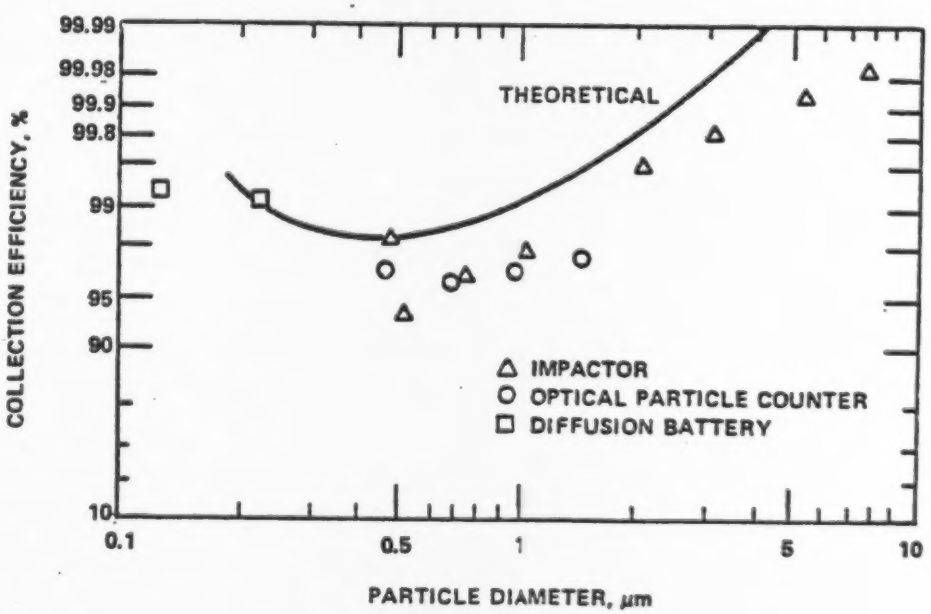


Figure 7-4. Measured and Computed Efficiency as a Function of Particle Size for a Hct-Side Electrostatic Precipitator at a Coal-Burning Power Plant [37].

electrode area per cubic meter per minute gas flow was calculated. This electrode area may not be large enough, however, to attain the design particulate removal efficiency of 95 to 98 percent because of such factors as the particulate discharging effect of polonium radiodecay on the particulate surface.

7.2.3 Venturi Scrubbers

Venturi scrubbers are classified as gas-atomized spray scrubbers. In a venturi scrubber the solid particles are collected on larger liquid drops, which are subsequently collected in an entrainment separator. Since the entrainment separator collects essentially 100 percent of the drops, the particle collection efficiency depends on what fraction of solids is collected on the drops. The collecting liquid (usually water) is injected into the venturi throat where the liquid is atomized. As the liquid drops are accelerated, the gas and particulates move past the drops. The differential velocity between the drops and particulates results in inertial impaction, which is the major particulate collection mechanism occurring in the venturi scrubber.

The performance of a venturi scrubber is summarized for air-water operation in a particulate-size specific penetration equation as follows [44]:

$$Pt = \exp\left(-0.006\, d_{pa}\Delta P\right)$$

where

Pt = fractional penetration (one minus efficiency)
d_{pa} = aerodynamic particle diameter (micron$\cdot(g/cm^3)^{0.5}$)
ΔP = venturi pressure drop (cm W.G.)

The aerodynamic particle diameter is calculated using the equation

$$d_{pa} = d_p(\rho_p C')^{0.5}$$

where

ρ_p = particle density (g/cm^3)
C' = Cunningham slip correction (dimensionless)

For a particle diameter of 0.5 micron with a density of 1.8 g/cm^3, the Cunningham slip correction is approximately 2, and the aerodynamic particle diameter is approximately 0.95 micron$\cdot(g/cm^3)^{0.5}$. A penetration of 0.05 (95 percent recovery) would result in

$$0.05 = \exp\left[-0.006\ (0.95)^2\ \Delta P\right]$$

In this instance, ΔP is the adjustable parameter and is equal to 554 cm W.G. Since the atmospheric pressure at the FMC plant is approximately 880 cm W.G., an exhaust pressure of 326 cm W.G. must be maintained. Because pressure losses would also be incurred in other related equipment, a design exhaust pressure of approximately 290 cm W.G. would be required.

This required operating pressure drop is significantly outside the normal operating range of venturi scrubbers. Typically, pressure drops are on the order of 200 cm W.G. [44]. The fractional particulate penetration increases as particle size decreases. For example, at a pressure drop of approximately 355 cm W.G., the penetration for a 1.0 aerodynamic particle diameter is 0.2. For a 0.5 aerodynamic particle diameter, the fractional penetration would be 0.3.

The process design equations for a venturi scrubber are not very sophisticated relative to the actual processes occurring in the scrubber. The simplifying assumptions involve many lumped parameter designations. Thus, actual data must always be available to make final assessments. The venturi design equations evolved through the 1970s from those in the 1972 Scrubber Handbook [44] to a venturi scrubber performance model described in the literature in 1978 [37]. The major change in the design equations during this time was the elimination of the adjustable parameter. But current state-of-the-art design equations still yield the same predictions in terms of fractional penetration versus particle size. These predictions show a rapid increase in penetration in the region below 1 micron particle diameter. Thus, the use of a venturi scrubber for particulates in this size region would be sensitive to specific conditions, and absolute performance predictions would not be possible. Therefore, using a venturi scrubber at the FMC and Monsanto-ID elemental phosphorus plants does not appear feasible because of the degree of fine particulate recovery required.

7.2.4 Novel Particulate Collection Devices

Considerable research has been conducted to understand and improve particulate recovery devices [45]. Various research projects include combinations of various particulate recovery mechanisms in systems such as electrostatic scrubbers. These devices can attain significantly improved recoveries for particulates smaller than 1 micron. Novel techniques and devices, such as the University of Washington Electroscrubber, Flux Force/Condensation Scrubbing, and an aspirating-type venturi scrubber [46], were not considered because they have not been applied to a process similar to that at the FMC or Monsanto-ID elemental phosphorus plants. The reliability of equipment scale up using the design equations is unknown, and there is virtually no cost history to use in developing cost estimates.

7.3 PROPOSED CONTROL ALTERNATIVES

Based on the evaluation, only barrier filtration and electrostatic precipitation appear suitable for controlling polonium emissions from the two out-of-compliance elemental phosphorus plants. These processes are essentially the only commercially available devices that can attain high particulate recovery efficiencies within the critical 0.1 to 1.0 micron diameter range. Other processes either do not exhibit the fine-particulate recovery efficiencies required or are virtual unknowns.

7.4 COST ESTIMATES

The cost estimates for the polonium emission control alternatives proposed for the FMC and Monsanto-ID plants were developed by assuming specific units would be added to the existing processes. Existing scrubbers and other equipment items would remain in line and provide fluoride control. The type of capital cost estimate provided here is termed an order-of-magnitude estimate [47], which is based primarily on unit capacity and is the least detailed of all recognized cost estimates. Typically, an order-of-magnitude cost estimate is considered to have an uncertainty of greater than $\pm$ 30 percent. The next more detailed cost estimate type is termed a study estimate and has an associated maximum uncertainty of approximately $\pm$30 percent. The study estimate requires estimates of engineering and drafting time, preliminary motor lists and sizes, preliminary flow sheet and specifications, rough flow quantities, approximate sizes and

types of construction, preliminary sizing and material specifications, and rough equipment sketches. Because of insufficient detailed data, this type of information could not be completely developed for the proposed polonium control unit operations at the FMC and Monsanto-ID elemental phosphorus plants.

The capital and operating cost estimates developed here are for adding either an electrostatic precipitator or a baghouse filter system to each of the FMC and Monsanto-ID plants. The cost estimates are based on gas stream flow rates of 8555 acmm (302,000 acfm) at Monsanto-ID and 13,530 acmm (477,800 acfm) at FMC. The unit operations sized and costed with these flow rates are an electrostatic precipitator at 0.79 m^2 of collecting electrode per cmm, and a baghouse with an air-to-cloth ratio of 4. Clearly, these basic sizing numbers could be in error because of a lack of basic data and the inability of the process design equations to yield absolute predictions of particulate recovery efficiencies in the region below 1 micron in particulate diameter. Thus, a required electrode area could be as high as 1.6 m^2/cmm, and the air-to-cloth ratio could be as low as 2.

Table 7-2 summarizes the costs developed for both plants. The capital costs presented are those to obtain an installed operating unit on a clean site and include necessary auxiliary equipment such as a fan, ducting, and a single stack. The retrofit costs presented pertain to the installed-unit capital cost for a site that contains existing equipment. Thus, the retrofit cost includes site preparation around existing equipment and is more than the capital cost for installed equipment on a clean site. Implementation costs include costs associated with startup, performance testing, model studies, and contingencies in startup. Operating costs include labor and power costs. Maintenance costs include labor and material replacement costs. For the baghouse operations, a one-year bag life was assumed because of an anticipated high humidity and fluoride corrosive environment. The costs presented in Table 7-2 were developed from basic cost data published in 1978 [48] and corrected to 1983 dollars.

Table 7-2. Cost Estimate Summary in 1983 Dollars.

	FMC		Monsanto-ID	
	ESP(1)	Baghouse	ESP	Baghouse
Capital	$14,096,000	$10,278,000	$10,490,000	$7,508,000
Retrofit Capital	15,564,000	11,529,000	11,582,000	8,423,000
Implementation	311,000	165,000	232,000	120,000
Operating(2)	87,000	503,000	69,000	294,000
Maintenance(2)	51,000	413,000	40,000	334,000

(1) Electrostatic precipitator

(2) Annual costs

8.0 CONCLUSIONS AND RECOMMENDATIONS

This study indicates that even after uncertainties are taken into account, the FMC and Monsanto-ID plants are clearly out of compliance with the proposed EPA standard. Also, the evaluation indicates that the probability of Po-210 emissions exceeding 1 Ci/yr is sufficient to classify the Monsanto-TN plant as being in borderline compliance.

Alternatives that could bring the borderline plant into compliance include establishing additional administrative controls and equipment additions or modifications. The proposed administrative controls involve decreasing polonium flow or diverting an existing flow within the plant. Equipment additions and modifications involve polonium recovery or diverting an existing flow within the plant. Cost estimates range from insignificant to several million dollars.

For the out-of-compliance plants, between 95 and 99 weight percent of all particulates between 0.1 and 1.0 micron must be removed from kiln scrubber stack emissions to meet the proposed standard. Only barrier filtration and electrostatic precipitation are capable of attaining these recovery efficiencies within the critical range. Estimated installed costs range from $7 to $11 million for an appropriately sized baghouse filter system and from $10 to $16 million for an electrostatic precipitation unit.

These results are preliminary and based on limited data, especially related to the transport of polonium. Costs are only order-of-magnitude estimates. Before more definite recommendations can be made, substantial information needs to be collected and analysis performed. Some of the problems yet to be resolved are discussed below.

Since the polonium data in this report were compiled primarily to estimate airborne emissions, these data are not readily applicable for determination of the rate of polonium transport. Measurement of polonium transport due to high-temperature volatilization would require different sampling points than those required to determine emissions.

Polonium emissions data were obtained by sampling and radioassay, assuming that the polonium resides on process particulates. Even though this assumption appears reasonable, the possibility exists that polonium is in a gaseous form at ambient temperatures as a result of chemical changes occurring in the calcining operation [31]. Available cascade impactor data suggest that this may be true. However, these observations have not been explained. If polonium is volatile at ambient temperatures after calcining, it is not possible to say that it is completely volatile. Thermodynamic considerations suggest that polonium will be present as a species that distributes between a gas phase and a solid (surface) phase.

What data are applicable and what data should be measured depend on whether the objective is to ensure compliance to a regulatory release limit or to determine polonium transport phenomena within the process. To ensure compliance with a release limit, pilot scale testing would be required on slip streams from each plant. Pilot testing would, however, provide relatively little understanding of polonium transport information. For pilot testing of an electrostatic precipitator, successful operation with respect to fractional polonium recovery could only be determined on a plant-specific basis. Applying the projected electrostatic precipitator performance to another plant would not be advisable because of varying particulate physical properties and size distributions.

To understand polonium transport, concentration measurements would be required around the calciner operations to determine the volatility of polonium. All such measurements would require an accurate sampling procedure that would relate to the volatility of polonium at ambient temperatures.

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APPENDIX A

DEVELOPMENT OF UNCERTAINTY STANDARD DEVIATIONS RELATED TO PO-210 EMISSIONS FROM FMC CALCINERS

A.1 SAMPLE COLLECTION EFFICIENCY

The relationship for the relative mass of material actually going up the stack as a function of the mass of material measured by the sampler is given by the relationship:

$$M_{SI} = M_{SR} [K_1 \exp(-K_2 R_v)]^{-1}$$

where

M_{SI} = stack particulate emission rate (g/sec)
M_{SR} = mass of sample removed by sampler (g/sec)
R_v = ratio of nozzle to stack velocity, u_s/u_a (dimensionless)
K_1 = 3.46 (dimensionless)
K_2 = 1.24 (dimensionless) (constants K_1, K_2 only apply in the range R_v = 0.3 to 2.0)

The standard deviation is calculated as

$$S(M_{SI}) = \left\{ K_1^{-2} e^{2K_2 R_v} S(M_{SR})^2 + K_1^{-2} M_{SR}^2 K_2^2 e^{2K_2 R_v} S(R_v)^2 + 2\rho \left[K_1^{-1} e^{K_2 R_v} \right] \left[K_1^{-1} M_{SR} K_2 e^{K_2 R_v} \right] S(M_{SR})\, S(R_v) \right\}^{1/2}$$

$$= \left\{ K_1^{-2} e^{2K_2 R_v} S(M_{SR})^2 + K_1^{-2} K_2^2 M_{SR}^2 e^{2K_2 R_v} S(R_v)^2 + 2\rho\, K_1^{-2} K_2 M_{SR} e^{2K_2 R_v} S(M_S)\, S(R_v) \right\}^{1/2}$$

The fractional standard deviation for the stack emissions is calculated using the formula:

$$F(M_{SI}) = \left\{ F(M_{SR})^2 + K_2^2 R_v^2 F(R_v)^2 + 2\rho\, R_v F(M_{SR})\, F(R_v) \right\}^{1/2} = 0.02838$$

A.2 RADIONALAYTICAL SAMPLE ANALYSIS UNCERTAINTY BASED ON INITIAL PO-210 ACTIVITY

Po-120 sample activity	pCi/m^3 = 1700 ± 140	= Q	F(Q) = 0.0412
Volume of sample	m^3 = 1.43	= V	
Sample flow rate	ft^3/min = 0.31 ± 0.15	= R	F(R) = 0.2419

Calculate the release rate activity, S_{AM} (pCi/sec) observed at sampler:

$$S_{AM} = \text{Po-210 (pCi/sec)} = Q \times V \times [V \times k_1 \times R^{-1} \times k_2]^{-1}$$

$k_1 = (0.0283\ m^3/ft^3)^{-1}$

$k_2 = 60$ (sec/min)

$$S_{AM} = Q \times R/[k_1 \times k_2] = k_3 \times Q \times R$$

$k_3 = 4.717 \times 10^{-4}$ (m^3-min/ft^3-sec)

The standard deviation is given by

$$S(S_{AM}) = \left\{k_3^2\ R^2\ S(Q)^2 + k_3^2\ Q^2\ S(R)^2\right\}^{1/2}$$

The fractional standard deviation is given as

$$F(S_{AM}) = [F(Q)^2 + F(R)^2]^{1/2}$$

The resulting mean release rate of Po-210 from the calciner 2-2 stack is

$$S_{AM} = 0.2466\ pCi/sec$$

Substituting values in the above equations:

	Low	High	Mean	SD	F_{SD}
R_v:	0.925	1.08	1.0025	0.1096	0.1093
M_{SR}:	4.797×10^{-6}	5.528×10^{-6}	5.162×10^{-6}	5.169×10^{-7}	0.1001

Consider interdependence of variables:

Correlation	$F(M_{SI})$
Independent, $\rho=0$	0.1688
Fully Dependent, $\rho=1$	0.2360

Use $\rho = 1$: $F(M_{SI}) = \underline{0.236}$ as uncertainty in sample collection efficiency.

with the overall uncertainty for radioanalytical/stack sample analysis:

$$F(S_{AM}) = 0.2454$$

Thus, the expected emission rate is

$$S_{AM} = 0.2486 \pm 0.1220 \text{ pCi/sec}$$

APPENDIX B

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